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THE NITROGEN INDUSTRY

BY

J. R. PARTINGTON, M.B.E.,
D.Sc. (Manc.),

AND

L. H. PARKER, M.A., D.S.C., F.I.C.

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CHEMICAL THERMODYNAMICS

AN INTRODUCTION TO GENERAL THERMODYNAMICS AND ITS APPLICATIONS TO CHEMISTRY

BY

J. R. PARTINGTON, M.B.E., D.Sc.(Manc.)

LATE FELLOW OF MANCHESTER UNIVERSITY

With 43 *Diagrams*

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PREFACE

When a new edition of my "Text-book of Thermodynamics with special reference to Chemistry" (1913) was called for, it seemed desirable that the treatment should be simplified as well as brought up to date. Practically every part has been rewritten, and in some cases alternative proofs have been given. The equations have, as far as possible, been stated in a form capable of direct numerical application, and many examples, with answers, have been provided. Some trouble has been taken in selecting what appeared to be the most accurate values of the constants and data given in the text, and many references to the literature of the subject, all, with one or two exceptions which proved inaccessible, verified with the originals, are given. The reader may in this way quickly turn up the recent (or standard) publications in any case where further information is required. A special feature is the inclusion of a good deal of recent work published in American journals, because it is particularly the countrymen of Willard Gibbs who have in recent years contributed most effectively to Chemical Thermodynamics. The accurate experiments, and the ingenious and original treatment, of the American workers on this subject will make all admit gratefully the debt which students in other countries owe to them. The examples quoted, however, are selected from the work of men of all nationalities, and a narrow outlook has been avoided as far as possible. The quotations are given in accordance with a list of abbreviations provided at the end of the book.

The symbols used are such as seemed most likely to be familiar to chemists, and most of the recommendations of the International Commission for the Unification of Physico-Chemical Symbols have been adopted. It is to be hoped that the further labours of this Commission will result in producing an adequate list of physico-chemical symbols acceptable by all workers. A list of the symbols used is also given at the end of the book.

With the object of saving space the numbers of the equations are given consecutively. Important equations are printed in black type. Equations which depend on the assumption of ideal gases are numbered in square brackets. Cross references are, for the same reason of economy of space, given to numbered equations or to paragraphs, the numbers of the latter appearing on the inside edges at the tops of the pages. A full index to pages is provided. The reader will usually find it helpful to make use of the cross references as though they formed part of the text where they occur. Repetition of equations would have increased the size of the book very materially.

I wish to acknowledge the valuable assistance I have received from my former students, Messrs. G. C. Attfield, B.Sc., and S. K. Tweedy, B.Sc. (who is responsible for most of the answers to examples), and from my colleague, Professor C. H. Lees, D.Sc., F.R.S., who very kindly looked through the proofs and made many useful suggestions. Mr. G. J. Wells, A.M.I.C.E., M.I.Mech.E., I must thank for most useful assistance with the new diagrams.

J. R. PARTINGTON.

LONDON,
February, 1924.

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CHEMICAL THERMODYNAMICS

CHAPTER I

Specific and Latent Heats

1. **True and Mean Specific Heats.**—Let a mass m of a given material be heated through a small temperature interval $\delta\theta°$.[1] The *heat absorbed* (taken positive) may be represented by:

$$\delta Q = mc \, . \, \delta\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where mc is the *heat capacity* of m, *i.e.*, the amount of heat absorbed per 1° rise in temperature under specified conditions (*e.g.*, constant volume, or pressure), and c is the *specific heat* (*i.e.*, the heat capacity of unit mass) under the given conditions.

For a finite rise in temperature from θ_1 to θ_2, the heat absorbed is:

$$Q = m\int_{\theta_1}^{\theta_2} c_\theta d\theta = m\bar{c}\,(\theta_2 - \theta_1) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

which gives a definition of $\bar{c}$, the *mean specific heat* over the interval of temperature $\theta_2 - \theta_1$; c_θ, which is called the *true specific heat* at the temperature θ, under the given conditions, may depend on the temperature, hence the suffix: $c_\theta = f(\theta)$.

If $\theta_2 - \theta_1$ is infinitesimally small:

$$\theta_2 - \theta_1 = (\theta + \tfrac{1}{2}\,\delta\theta) - (\theta - \tfrac{1}{2}\,\delta\theta) = \delta\theta,$$

then, for unit mass ($m = 1$), under the specified conditions,

$$c_\theta = \lim_{\delta\theta \to 0} \frac{\delta Q}{\delta\theta} = \frac{dQ}{d\theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

---

[1] The symbol θ is used throughout to denote temperature measured on *any* scale, unless the scale is specified.

We see from (2) that:

$$\bar{c} = \frac{1}{\theta_2 - \theta_1}\int_{\theta_1}^{\theta_2} c_\theta d\theta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

hence $\bar{c}$ is the *mean value* of c_θ over the range $\theta_2 - \theta_1$.

If we adopt a graphical representation ($x = \theta$, $y = c_\theta$) we see that $\int c_\theta d\theta$ is proportional to the heat absorbed, and is represented by the area $AB\theta_2\theta_1$ (Fig. 1). If we draw EF horizontal and at such a height that:

$$\text{area } EF\theta_2\theta_1 = \text{area } AB\theta_2\theta_1,$$

then[1] the ordinate of EF represents $\bar{c}$.

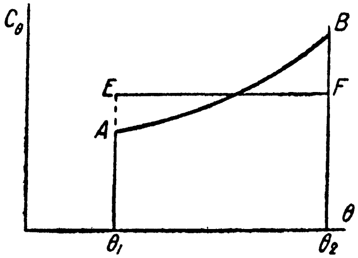

FIG. 1.

2. Change of Specific Heat with Temperature.—We can evaluate $\int c_\theta d\theta$ only if we know the dependence of c_θ on θ, *i.e.*, c_θ as a function of θ. c_θ may depend on other variables besides θ, *e.g.*, on pressure (this is the case with c_v and c_p for *actual* gases, cf. §§ 31, 36), or change of composition on heating (§ 89).

The dependence of c_θ on θ we can obtain:

(1) *Theoretically.*—For example:

(*a*) From the Kinetic Theory of Gases we know that for a mol M of an ideal monatomic gas, such as argon, at constant volume, Mc_v has the value 2·98 gm. cal., and is independent of temperature.

(*b*) From the Quantum Theory (see Chapter XVIII.) different forms of the function $c_v = f(\theta)$ for a monatomic solid, such as silver, may be found.

(2) *Experimentally.*—This is the most usual method, but is difficult, since specific heats alter only slightly with temperature over moderate intervals. As a first approximation c is usually regarded as a constant. From the experimental result that c varies only slowly with temperature, we can express its dependence in the form of a power series[2]:

$$c_\theta = f(\theta) = a + b\theta + c\theta^2 + d\theta^3 + . \quad . \quad . \quad . \qquad (5)$$

where $a = f(0) = c_0$ for $\theta = 0$, say at the freezing-point of water.

The *unit of heat* is defined by equation (2) by making the true specific heat of some standard substance equal to unity under specified conditions. If (i.) the gram is the unit of mass, (ii.) $\theta_2 - \theta_1 = 15\frac{1}{2}^\circ$ C. $- 14\frac{1}{2}^\circ$ C., and (iii.) water is the standard substance, then Q is defined as the 15° *gram-calorie*, which we shall adopt as the unit of heat, and denote simply by " cal."

---

[1] See *H. M.*, p. 125.

[2] *H. M.*, p. 171.

A *definite* interval of temperature, $\theta_2 - \theta_1 = 1$, must be chosen, since c varies with temperature. At 15° C. the specific heat of water is 1, but at other temperatures, if Q is still measured in 15° calories, the specific heat of water will no longer be unity.

According to the measurements of Rowlands (1880), Bartoli and Stracciati (1892), Lüdin (1895), Callendar and Barnes (1902), and Dieterici (1905), the true specific heat of water in terms of the 15° calorie is as follows,[1] temperatures being measured on the hydrogen thermometer:

θ°C.	0	5	10	15	20	25	30
c	1·008	1·005	1·0013	1·0000	0·999	0·998	0·998

At temperatures higher than 30°, the results of Barnes give:

$$37{\cdot}5° \text{ to } 55°:\quad 0{\cdot}99733 + 3{\cdot}5 \times 10^{-6}(\theta - 37{\cdot}5)^2 + 10^{-7}(\theta - 37{\cdot}5)^3$$
$$55° \text{ to } 100°:\quad 0{\cdot}99850 + 1{\cdot}2 \times 10^{-4}(\theta - 55) + 2{\cdot}5 \times 10^{-7}(\theta - 55)^2.$$

The latest measurements made at the German Reichsanstalt (Holborn, Scheel and Henning, " Wärmetabellen," 1919) give:

θ° C.	0	5	10	15	20	25	30
c	1·005	1·0030	1·0013	1·0000	0·9990	0·9983	0·9979

in excellent agreement with the results given above.

If $\theta_2 = 100°$ C., $\theta_1 = 0°$ C., then Q/100 is defined as the *mean calorie*, the value of which has been variously estimated at 0·03 to 0·2 per cent. larger than the 15° calorie; it may be taken as equal to the latter. The *zero calorie* (0° − 1°) is 1·005 times the 15° calorie.[2]

It is usually sufficient in series (5) to take terms up to θ^2 only (in the accurate equations for the specific heat of water given above, terms up to θ^3 are included):

$$c_\theta = a + b\theta + c\theta^2,$$

or, with a more convenient notation,

$$c_\theta = c_0 + a\theta + b\theta^2 \ (c_0 = \text{constant}).$$

$$\text{Then } Q/m = \int_{\theta_1}^{\theta_2} c_\theta d\theta = \int_{\theta_1}^{\theta_2} (c_0 + a\theta + b\theta^2)\, d\theta$$
$$= c_0(\theta_2 - \theta_1) + \tfrac{1}{2}a(\theta_2^2 - \theta_1^2) + \tfrac{1}{3}b(\theta_2^3 - \theta_1^3) \quad . \quad (6)$$

Put $\theta_1 = 0$, $\theta_2 = \theta$, then:

$$Q/m = c_0\theta + \tfrac{1}{2}a\theta^2 + \tfrac{1}{3}b\theta^3.$$

From (4) when $\theta_1 = 0$: $\bar{c} = \dfrac{1}{\theta}\displaystyle\int_0^\theta c_\theta d\theta \quad \therefore \quad \bar{c}\theta = \int_0^\theta c_\theta d\theta.$

Differentiate both sides with respect to θ:

$$d(\bar{c}\theta)/d\theta = c_\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

---

[1] Nernst, " Theoret. Chem.," 8–10 aufl., p. 12.

[2] Cf. Romberg, *Proc. Amer. Acad. Arts and Sci.*, 1922, 57, 377, for the ratio of the calorie at 73° to that at 20°.

To find the true specific heat from the mean specific heat over a range of θ reckoned from zero, multiply the mean specific heat by θ and differentiate with respect to θ.

Conversely, *to find the mean specific heat from the true specific heat, integrate the latter over the desired range of temperature, and divide by the range of temperature.*

3. The Specific Heats of Gases.—The methods used in the determination of the specific heats of gases at moderate temperatures are described in text-books of physics (*e.g.*, Preston). Usually the *specific heat at constant pressure* (unless otherwise stated, 1 atmosphere), c_p, is determined, and the value of the *specific heat at constant volume*, c_v, is calculated from this, either (i.) from the value of the *difference of the specific heats* $(c_p - c_v)$, which can be calculated from the characteristic equation of the gas (Chapter VIII.), or (ii.) from the value of the *ratio of the specific heats* $c_p/c_v = \gamma$, which may be measured by the cooling of the gas on adiabatic expansion (§ 37), or from the velocity of sound in the gas (§ 38).

The direct measurement of c_v by Joly's method, in which the weights of steam condensed on a copper globe filled with gas under pressure and on a vacuous copper globe, suspended from the two arms of a balance, are compared, is very difficult to carry out so as to give accurate results.[1]

The specific heats of gases at constant volume at low temperatures have been measured by Eucken.[2]

The *specific heats of gases at high temperatures*, at constant volume, have been determined by an *explosion method*.[3] A known amount of detonating gas $(2H_2 + O_2)$ is mixed with a known amount of an inert gas (*e.g.*, H_2, O_2, A, but not Cl_2 or N_2) and exploded by an electric spark in a strong steel bomb. The heat evolved is allowed to pass into a water bath in which the bomb is immersed, and can be measured. This heat, Q, is primarily imparted to the water vapour produced by the explosion and to the inert gas. If the temperature immediately after the explosion is θ_2, and if θ_1 is the temperature to which the system is afterwards cooled in the water bath, then:

$$Q = (\theta_2 - \theta_1)(m_1\bar{c}_1 + m_2\bar{c}_2),$$

---

[1] *P. R. S.*, 1886, **41**, 352; *ibid.*, 1889, **47**, 218; *P. T.*, 1892, **182**, 73; *ibid.*, 1894, **185**, 943.

[2] *B. B.*, 1912, p. 151.

[3] M. Pier, *Z. E.*, 1909, **15**, 536; 1910, **16**, 897; *Z. p. C.*, 1908, **62**, 397; N. Bjerrum, *ibid.*, 1912, **79**, 513, 537; W. Siegel, *ibid.*, 1914, **87**, 641; cf. Jellinek, "Lehrb. der physikalischen Chemie," vol. 1, pp. 182–190, 1914.

a correction being applied for the latent heat of condensation of the steam. In this equation, m_1 and m_2 are the masses of the steam and of the inert gas, and $\bar{c}_1, \bar{c}_2$, the mean specific heats. It is assumed that $\bar{c}_1$ (or $\bar{c}_2$) is known. The value of θ_2 is found from the pressure p_2, developed in the explosion :

$$p_2/p_1 = (\theta_2 + 273)/(\theta_1 + 273)$$

where p_1 is the initial pressure (a correction being applied to p_2 for the change of volume due to the reaction $2H_2 + O_2 = 2H_2O$).

The determination of the maximum pressure during the explosion is a matter of no small difficulty. Older workers[1] had made use of a piston confined by a spring, but this moves much too slowly, and gives too low values for the maximum pressures. Pier used a fairly thin corrugated steel membrane covering a hole in the bomb, and reflected a beam of light from a mirror attached to the membrane. By registering the reflected beam on a rotating drum of sensitive film, he obtained a sharp maximum of pressure instead of a rounded peak as in the older observations. Vibrations of the membrane, and explosion waves, must be avoided. An accuracy of about 1 per cent. is claimed, but it is doubtful if this was attained.

By means of such measurements the following values for the true molecular heats in gm. cal. at constant volume were found (the table includes older measurements by Regnault, Wiedemann and Strecker ; it was compiled by Nernst,[2] and takes no account of small differences exhibited by gases such as N_2 and O_2, SO_2 and CO_2) :

	0°	100°	300°	500°	1200°	2000°
A	2·98	2·98	2·98	2·98	3·0	3·0
I	—	—	—	—	3·0	3·0
N_2, O_2, HCl, CO . .	4·90	4·93	5·17	5·35	5·75	6·22
H_2	4·75	4·78	5·02	5·20	5·6	6·0
Cl_2	5·85	5·88	6·12	6·30	6·9	7·4
H_2O	5·93	5·97	6·45	6·95	8·6	12·1
CO_2, SO_2	6·80	7·43	8·53	9·43	11·1	11·5
NH_3	6·62	6·82	7·41	8·52	—	—
$(C_2H_5)_2O$	*c.* 32	32·6	41·6	—	—	—
Air[3]	4·95	4·99	5·02	5·13	—	—

---

[1] For a summary of the older work, see Haber's "Thermodynamics of Technical Gas Reactions," transl., 1908, ch. 6.

[2] *P. Z.*, 1912, **13**, 1064 ; cf. *Z. E.*, 1911, **17**, 272 ; cf. Partington, *F. S.*, 1922, **17**, 734.

[3] Partington and Shilling, *F. S.*, 1923, **18**, 386 ; *Engineering*, 1923, Jan. 19th, p. 82 ; Dixon, Campbell and Parker, *P. R. S.*, 1920, **100**, 1.

Except in the case of monatomic gases (and even in this case there may be a slight increase at very high temperatures, and in the case of helium perhaps a slight decrease below 2·98 at very low temperatures),[1] the specific heat in all cases increases with rise of temperature, the increase being more rapid the more complicated the molecule of the gas. The significance of this will be considered later (see § 127).

4. **The Specific Heats of Solids.**—The methods used in the determination of the specific heats of solids at moderate temperatures are described in text-books on heat (*e.g.*, Preston's). The *specific heats of solids at very low temperatures* are of importance in connection with the Quantum Theory, and a brief account of the methods used may be given here.[2]

The *copper calorimeter* consists of a weighed block of copper placed inside a Dewar tube. There is a hole bored in the block, and a thermocouple is also inserted in the block, in good contact with it. A known mass of the substance, at a known temperature, is dropped into the cavity of the block, the latter having first been cooled to a known temperature by immersion in liquid air. The rise in temperature is measured by the thermocouple, and the *mean specific heat* of the substance calculated in the usual way.

In the *vacuum calorimeter*, a block of the substance itself, or a small silver vessel containing the substance, is furnished with a heating coil of platinum, carrying an electric current. The resistance of this coil at the same time gives a measure of the temperature. The block is hung by fine wires inside a glass vessel which is exhausted to as low a vacuum as possible, to eliminate loss of heat by conduction or convection. Loss by radiation is negligible at very low temperatures. The material is first cooled to a low temperature by immersing the apparatus in liquid air or liquid hydrogen, a little hydrogen being left in the glass vessel to conduct away the heat until the required low temperature is reached, when as good a vacuum as possible is established. By the addition of successive small quantities of heat, and measurement of the resulting rises in temperature, the true specific heats over a wide range of temperatures can be found. At very low temperatures, a resistance thermometer of lead instead of platinum is used.

---

[1] Cf. Partington, *F. S.*, 1922, **17**, 734.

[2] For details see Simon, *A. P.*, 1922, **68**, 241; Nernst, *A. P.*, 1911, **36**, 395; "Theory of the Solid State," London, 1914; "Die Grundlagen des neuen Wärmesatzes," 1918; Jellinek, "Lehrb. d. physik. Chem.," vol. 2, pp. 483–509; Arndt, "Handbuch der physikalisch-chemischen Technik," 1915, pp. 453–466; Lewis, "A System of Physical Chemistry," 1921, vol. 3; Harper, *Sci. Paper Bur. Stand.*, Washington, 1915, No. 231; K. Onnes and Keesom, *Communications of Leyden Lab.*, No. 143 (1914), and *A. A.*, 1916, **18**, 1247, and later papers; Griffiths. *P. T.*, 1913, **213**, 119; 1914, **214**, 319.

The very remarkable result of these measurements was the great drop in the specific heats of solids at very low temperatures, which had previously been established by experiments of Dewar. This is evident from the curves in Fig. 2, giving the *atomic heat* = specific heat × atomic weight, as a function of absolute temperature. Its significance will be discussed later (§ 130) in connection with the Quantum Theory. According to Richarz an allotropic form with the higher specific heat has the smaller density, but this does not appear to hold for tin.[1]

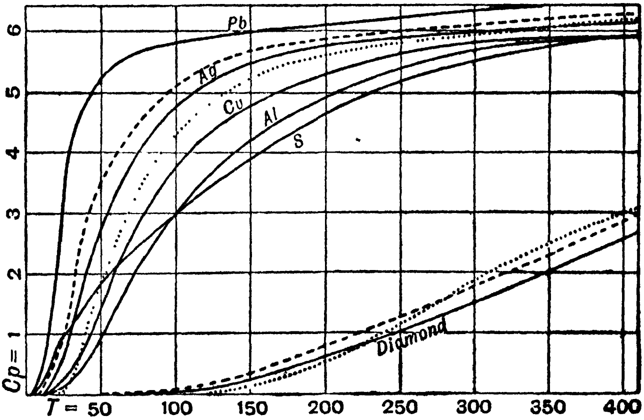

FIG. 2.

From Partington's "Inorganic Chemistry," by permission of Messrs. Macmillan.

5. **Latent Heats.**—In some cases the definition of Q by equation (2) fails, since Q is finite whilst $\theta_2 - \theta_1$ is zero. Heat absorbed by a body at constant temperature is called *latent heat.* In such cases, *e.g.*, in the liquefaction of ice at 0° C., the heat absorbed by the system must be measured by the fall in temperature of some other system supplying the heat (*e.g.*, hot water), or by the energy equivalent of heat supplied by an electric current passing through a resistance coil.

[1] Wigand, *Z. E.*, 1914, **20**, 38; specific heats *at very high temperatures*, White, *A. J.*, 1919, **47**, 44; Latimer, *J. A. C. S.*, 1922, **44**, 2136. Worthing gives the following values for the atomic heats of tungsten and carbon at high temperatures: tungsten, at 927° C., 6·25; at 2127° C., 7·35; carbon, at 927° C., 5·35, and at 1727° C., 6·05 (*F.*, 1918, **185**, 707). This shows that atomic heats exceed the value 3R at high temperatures. See also Magnus, *A. P.*, 1915, **48**, 983.

There are two important latent heats, corresponding with the changes of physical state of unit mass of a pure substance at a definite temperature, usually the melting or boiling point under 1 atm. pressure, viz., the *latent heat of fusion*, denoted by L_f, and the *latent heat of evaporation*, denoted by L_e. The methods of determining these will be found in the text-books on heat; only one method for determining the latent heat of fusion will be described, which differs from previous methods in that it does not necessitate a knowledge of the specific heats of the solid and liquid.[1]

To a weighed amount of the substance, contained in a calorimeter, a known amount of heat is supplied by an electrical resistance coil immersed in the substance, which is initially at the melting point, but is wholly solid. This condition is ensured by immersing the calorimeter in a bath of fused substance containing some solid. The temperatures of the bath and calorimeter are always equal, so that no heat transfer occurs. When the temperature in the beaker on heating with the coil just begins to rise, all the solid is fused, and if C is the (constant) current in ampères, R the resistance of the coil in ohms, and t the time in seconds during which heat is supplied :

$$L_f = C^2Rt/4{\cdot}2\,m \text{ gm. cal.,}$$

where m is the mass of the substance.

EXAMPLES I.

1. Find the mean specific heat of iron over the range of temperature 100° C. — 200° C. if the true specific heat is (Pionchon) $c = 0{\cdot}11012 + 0{\cdot}0000506\,\theta + 0{\cdot}0_6164\,\theta^2$, which holds from 0° C. — 660° C.

2. The mean specific heat of copper is $0{\cdot}0939 + 0{\cdot}00001778\,\theta$ between 15° and its melting point. Find the total heat which would be given out when 1 kilogram of melted copper is cooled from its melting point, 1065°, to 15°. The latent heat of fusion is 43 cals. per gram.

3. According to Magnus (1915) the heat evolved when 1 gm. of platinum cools from T to T_0 is

$$Q = 0{\cdot}031590\,(T - T_0) + 2{\cdot}9234 \times 10^{-6}\,(T^2 - T_0^2).$$

Find an expression for the mean specific heat of platinum, $\bar{c}$, between the temperatures T_0 and T. Find also an expression for the true specific heat at temperature T and calculate its value at 30° C. (T is temperature in degrees absolute; $T = \theta° \text{ C.} + 273$.)

4. Assuming C_p (true) for H_2 to be $6{\cdot}50 + 0{\cdot}0009\,T$, find the heat absorbed when 50 gm. of H_2 are heated from 0° C. to 500° C.

5. If the mean specific heat of carbon dioxide is (Holborn and Austin) $\bar{c}_p = 0{\cdot}2028 + 0{\cdot}0_4692\,\theta - 0{\cdot}0_7167\,\theta^2$, find the true specific heat at 500° C., and obtain a formula for the true molecular heat in terms of absolute temperature ($T = \theta + 273$).

---

[1] K. Stratton and J. R. Partington, *P. M.*, 1922, **43**, 436. For other values of L_f see table in § 135. Latent heats of gases at low temperatures, see Eucken, *B. P.*, 1916, **18**, 4; Mortimer, *J. A. C. S.*, 1922, **44**, 1416.

6. Naccari (1887) gives the following expressions for the true specific heats of some metals at a temperature t° C:

Cu . . . $c = 0{\cdot}092 + 0{\cdot}0_4 2125\, t$.
Pb . . . $c = 0{\cdot}0297 + 0{\cdot}0_4 1358\, t$.
Zn . . . $c = 0{\cdot}0907 + 0{\cdot}0_4 4440\, t$.
Cd . . . $c = 0{\cdot}0546 + 0{\cdot}0_4 2367\, t$.

Calculate in each case the mean specific heat over the range 0°—100° C.

7. Find the heat absorbed on heating 100 grams of CO_2 from 15° to 1000° C. at constant volume if the true molecular heat at constant volume is $C_v = 6{\cdot}50 + 0{\cdot}00193\,\theta$.

8. The true specific heats per 1 gram for CO_2 at constant pressure (Wiedemann) are:

0°		100°		200°
0·1952	...	0·2169	...	0·2387

Find a formula for the true molecular heat from 0° to 200° C., the mean molecular heat between 100° and 200° absolute, and the total heat given out on cooling 1 mol from 200° to 0° C.

9. C_p for water vapour up to 2000° C. is $8{\cdot}81 - 1{\cdot}9\,.\,10^{-3}\,T + 2{\cdot}22\,.\,10^{-6}T^2$. Find the mean molecular heat between 100° and 1000° C.

10. Holborn and Henning (1905) give for the mean $\bar{c}_p$ of steam in terms of that of air as unity, the following values:

110°—270° C., 1·940; 110°—440° C., 1·958; 110°—620° C., 1·946; 110°—820° C., 1·998. Assume the value $\bar{c}_p = 0{\cdot}2355\,(1 + 0{\cdot}0_4 4\,\theta)$ for air and find an equation for the mean $\bar{c}_p$ for steam and the true specific heat at 350°.

11. Holborn and Jacob[1] find the specific heat of air at 59° under p atm. pressure (1—200 atm.) as: $10^4\, c_p = 2413 + 2{\cdot}86\, p + 0{\cdot}0_3 5\, p^2 - 0{\cdot}0_4 1\, p^3$. Find the value of $(\partial c_p / \partial p)_T$ at 100 atm.

12. A flue gas leaving a chimney at 230° C. had the composition by volume CO_2 8%, CO 4%, O_2 8%, N_2 80%. Find the heat carried away by the gas per *cb. m.*, referred to the standard temperature 15° C., assuming the data given in (8) and $C_p\,(O_2, N_2, CO) = 6{\cdot}50 + 0{\cdot}001\,T$.

13. A mixture of excess chlorine and hydrogen was exploded in a Pier bomb. The initial temperature of the mixed gases was 0° C. and the partial pressure of the Cl_2 is 0·655 atm. The maximum pressure registered on explosion was 3·74 atm. Calculate $\bar{C}_v$ for Cl_2 if only 1 mol of HCl is formed, given that Q for HCl is 22,000 cals. (evolved) and that $\bar{C}_v$ for HCl $= 4{\cdot}900 + 0{\cdot}00045\,\theta$.

14. The true specific heat of aluminium is given by the formula $c = 0{\cdot}2116 + 0{\cdot}00009507\,\theta$ (θ° C.). Al melts at 658·5° C. and its latent heat of fusion is 61 cals. per gram. Calculate the heat required to fuse 500 gms. Al from 25° C.

15. The mean molecular heat at constant pressure of water vapour at any temperature may be taken from the formula: $\bar{C}_p = 5{\cdot}8 + 0{\cdot}0029\,\theta$. Find $\bar{C}_p$ between 100° and 200°; also the amount of heat given out by 1 mol of water vapour in cooling from 200° to liquid water at 0° at constant pressure if $L_e = 537$ gm. cal. per gm.; c_p (liquid from 0° to 100°) = 1·0.

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[1] *B. B.*, 1914, 213.

CHAPTER II

The First Law of Thermodynamics

6. The Mechanical Equivalent of Heat.—It is a matter of observation that *work* expended against friction is converted into *heat.* If a measured amount of work A is expended in stirring water, the quantity of heat Q produced is found from the rise in temperature of the water. The ratio A/Q is called *the mechanical equivalent of heat,* denoted by J.

The value of J depends upon the units in which A and Q are measured. If we take the *erg*[1] as *the unit of work,* and the 15° *calorie* as the *unit of heat,* the mechanical equivalent of heat is the number of ergs of work which must be completely expended in stirring water such that the temperature of 1 gram of water is raised from 14½° C. to 15½° C. It is found that $J = 4{\cdot}1842 \times 10^7$ ergs.[2]

In other units, the value of J is, of course, different. Thus, if Q is measured in gram calories and A in gram-centimetres, J = 42,670. The value of J is known with an accuracy probably not greater than 1 part in 1000.

J. P. Joule in 1843 made the important discovery that the value of J was independent of the method in which work is converted into heat, and depends solely on the units of heat and work. If A units of work are converted completely into heat, and Q units of heat are produced, then :

$$A = JQ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where J is a constant, the mechanical equivalent of heat. With suitable units for A and Q, we can make J = 1, and in that case :

$$A = Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

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[1] The *erg* is the work done by a force of 1 *dyne* moving its point of application through 1 cm. The *dyne,* or C.G.S. unit of force, is that force which imparts to a mass of 1 gram an acceleration of 1 cm. per sec. per sec. The *dimensions* of force and energy are $[mst^{-2}]$ and $[ms^2t^{-2}]$, respectively, where m = mass, s = length, t = time.

[2] Physikalisch-technische Reichsanstalt "Wärmetabellen," 1919; mean of previous results is $J = 4{\cdot}186 \times 10^7$ ergs per 15° cal. Cf. Winkelmann, "Physik," III., 537 ff.; A. W. Smith, *P. R.,* 1911, 33, 173.

It is convenient to adopt work units (ergs) as fundamental, and in that case quantities of heat are measured in work units when equation (8a) is used. Unless otherwise stated quantities of heat will be assumed in future to be measured in work units, and care must be taken in using the equations that the physical magnitudes are expressed in corresponding units.

The experiments of Joule were begun in 1840[1]; the first series was published in 1843,[2] giving J = 459·62 gm. m. per cal. The second series, also in 1843, corrected in 1845,[3] gave 424·6. The third series, comprising the well-known water-stirring experiments, was made, and the results published, between 1845 and 1849[4]; the result was 424·3. In 1844[5] he measured the heat of compression of a gas, finding 436·1; in the same year the cold produced by expansion gave 448·2. These were not considered accurate. The electric calorimeter method was published in 1867,[6] giving J = $4{\cdot}167 \times 10^7$ ergs per 15° cal. The last series of experiments, on water stirring, which gave $4{\cdot}171 \times 10^7$, was made in 1878.[7] When Nernst[8] speaks of "the fundamental researches of Joule (1850)," after mentioning Mayer[9] (1842) and Helmholtz[10] (1847), it appears as though he has not quite done justice to the former. Neither Mayer nor Helmholtz made any experiments. Mayer's claims have repeatedly been urged.[11] Lippmann[12] repeats the mistake of Bertrand.[13]

7. Energy.—The simplest interpretation of Joule's results is to assume that heat and work are merely different forms of some physically real entity called *energy* (ἡ ἐνέργεια),[14] which is conserved in all transformations between the two forms. This is rendered probable by the fact that there are other entities besides work which can be converted into heat in accordance with equation (8). It is convenient to measure ultimately all forms of energy in work units, say in ergs, and *energy* may be defined as work or anything which is produced from, or can be converted into, work. The following *forms of energy* have been recognised: potential energy and kinetic energy of mechanical systems ; heat ; radiation ; chemical energy ; atomic or radioactive energy ; electrical energy ; magnetic energy ; surface energy.

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[1] *P. T.*, 1850, **140**, 63.

[2] *P. M.*, 1843, **23**, 263, 347, 435, "On the Calorific Effects of Magneto-Electricity and on the Mechanical Value of Heat." The numerical values are recalculated by Graetz, Winkelmann's "Physik," III., 540 ff.

[3] *P. M.*, 1845, **27**, 205, "On the Existence of an Equivalent Relation between Heat and the Ordinary Forms of Mechanical Power."

[4] *P. M.*, 1845, **27**, 205. "On the Existence of an Equivalent Relation between Heat and the ordinary Forms of Mechanical Power"; *ibid.*, 1847, **31**, 173, "On the Mechanical Equivalent of Heat as determined by the Heat evolved by the Friction of Fluids"; *C. R.*, 1847, **25**, 309; *P. T.*, 1850, **140**, 61, "On the Mechanical Equivalent of Heat."

[5] *P. M.*, 1845, **26**, 369, "On Changes of Temperature produced by the Rarefaction and Condensation of Air."

[6] *B. A.*, 1867, i., 512.

[7] *P. T.*, 1878, **168**, 365.

[8] "Theoret. Chem.," 8–10 Aufl., 1921, p. 11.

[9] *A.*, 1842, **42**, 233: The "law" was obtained as follows: "Kräfte sind Ursachen, mithin findet auf dieselbe volle Anwendung der Grundsatz; *causa æquat effectum.* Hat die Ursache *c* die Wirkung *e*, so ist *c* = *e*." See the confused ideas on pp. 236, 238, 239 of Mayer's paper.

[10] Helmholtz, "Über die Erhaltung der Kraft," Berlin, 1847; Ostw. Klass., No. 1.

[11] See especially Tyndall, *P. M.*, 1864, **28**, 25. In a MS. note to his copy of this paper, in my possession, Tyndall adds: "It might have been well had the blood run less warmly through these pages. J. T."

[12] "Abhandl. und Vorträge," 1906, i, 551; see, however, *Chem. Z.*, 1923, **47**, 807.

[13] Cf. § 19.

[14] The result of the theory of relativity that the energy U has a mass *m* given by the equation $U = mc^2$, where *c* is the velocity of light, prevents our saying that "energy is immaterial." See Cunningham, "Relativity and the Electron Theory," 1921, p. 80.

Chemical energy is energy a system possesses which is capable of liberation as heat (or some other form of energy), as a result of chemical changes which the system may undergo.

We have no means of *measuring* the absolute amount of energy associated with a system, but only the changes of energy when the system undergoes changes of state.

With the metaphysical significance of energy we are not concerned : the definitions have been framed so as to avoid it as far as possible.

8. The First Law of Thermodynamics.—The truth of the following statement is assumed :

It is impossible to construct a machine which shall produce no other effects than the generation or destruction of mechanical work, or anything equivalent to mechanical work, i.e., of any form of energy.

A machine which would produce or destroy [1] unlimited quantities of work without producing any other changes would constitute a *perpetual motion.* As a result of the failure of numerous attempts in former years to construct such a machine we may assert that the above statement has been arrived at by experiment. It is called the *First Law of Thermodynamics.*

Before Joule's experiments, begun in 1840, heat was generally regarded as an imponderable material substance, and called *caloric.*[2] Many suggestions had been made, however, that it was really a "form of motion,"[3] *i.e.*, the same in essence as kinetic energy. Experiments of Rumford in 1798,[4] and of Davy[5] in 1799, had shown that heat could be produced in unlimited amounts by friction, and the value of J calculated from Rumford's experiments differs by only about 10 per cent. from the accepted value. The particular form of the dynamical theory of heat which identifies the energy of a gas with the kinetic energy of its molecules was foreshadowed by Bernoulli.[1]

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[1] "Spurlos versenken."

[2] On earlier theories of heat see Boerhaave, "Elementa Chemiae," Leyden, 1732, Vol. I., pp. 126 ff.; Black, "Lectures on the Elements of Chemistry," Edinburgh, 1803, Vol. I., pp. 30 ff., 117, 157. Also Scheele, "On Air and Fire," Eng. tr., 1780. The name *caloric* is due to Lavoisier, "Elements of Chemistry," tr. 1796, p. 53.

[3] First by Lord Bacon in *Novum Organum*, Eng. tr. of Works, London, 1901, vol. 4, p. 154.

[4] *P. T.*, 1798, 88, 80.

[5] "Essay on Heat and Light," *Works*, vol. 2, p. 11.

Although the failure of perpetual motion apparatus to *produce* energy from nothing may be regarded as a firmly established experimental fact, the converse case of the *destruction* of energy is perhaps not so directly demonstrated.

9. **Cyclic Processes.**—A system which, after any process or series of processes (changes), returns to its initial state, is said to have undergone a *cyclic process* (or a *cycle of changes*).

The important conception of a cyclic process is due to Sadi Carnot.[2]

Let Q units of heat be *absorbed* by the system and A units of work be *done by* the system in the cycle. Since no other energy changes occur (cycle), these two are equivalent: $A = Q$. If this were not the case, the given cycle could, by repeated execution, produce or destroy unlimited quantities of energy without any other changes occurring, which is impossible.

If the change is not cyclic, *i.e.*, the initial and end states are different, no relation between A and Q can be written down *a priori*. We shall suppose that in this case A and Q have been separately determined by experiment. Two cases are possible:

I. $A = Q$, although the process is not cyclic. A process of this kind we shall call an *aschistic process* (*a*, not; σχίζω, I divide). The expansion of an ideal gas at constant temperature will be shown (§ 33) to be such a process.

II. A is not equal to Q. This is the general case.

If we exclude the possibility of other energy changes outside the system, and if the First Law of Thermodynamics is true, there must in Case II. have been some energy change in the system itself. We *define* this as the change of *intrinsic energy* of the system, as follows:

$$Q - A = U_2 - U_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where U_1 and U_2 are the intrinsic energies of the system before and after the change. If the heat and work changes occur in different parts of the system, or at different times, either simultaneously or separately, we can write (9) in the form:

$$\Sigma Q - \Sigma A = U_2 - U_1 = \Delta U \quad . \quad . \quad . \quad . \quad (10)$$

Equations (9) and (10) are *merely definitions* of the increase of intrinsic energy $(U_2 - U_1)$, and give no information as to the separate values of U_1 and U_2. The intrinsic energy was first described by Lord Kelvin.[1]

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[1] "Hydrodynamica," Strasburg, 1738, p. 202.

[2] "Réflexions sur la puissance motrice du feu, et sur les machines propres à développer cette puissance," 1824; reprinted and translated, cf. § 25.

10. The Principle of Conservation of Energy.—*The change of intrinsic energy of a system undergoing any change of state depends solely on the initial and final states of the system and is independent of the manner in which the change from one state to the other is effected.*

Let the change from the initial state A to the final state B be carried out along the path M (Fig. 3), and let the increase of intrinsic energy be ΔU_M. Then let the change be reversed by carrying the system from the state B to the state A along another path, N. Let the increase of U be $-\Delta U_N$. The two changes constitute a cycle, hence the total change of U is zero. Thus $\Delta U_M - \Delta U_N = 0$, or $\Delta U_M = \Delta U_N$.

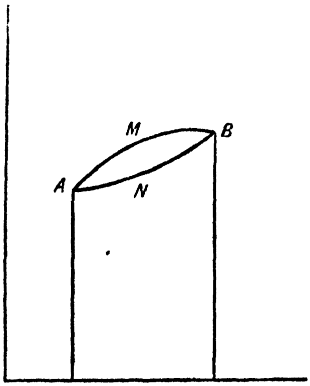

FIG. 3.

The same method may be applied to any other possible direct change instead of M, but the proof depends on the existence of at least one path (N) along which the change from A to B can be reversed. If this does not exist (*e.g.*, radioactive changes) the principle can only be inferred.

If Q and A are very small we may write (9) as:

$\delta Q - \delta A = dU$, and for a finite change:

$$\int \delta Q - \int \delta A = \int dU = U_2 - U_1 \quad . \quad . \quad . \quad . \quad (11)$$

If the change is a cyclic process:

$$(\int) \delta Q - (\int) \delta A = (\int) dU = 0$$

or

$$(\int) \delta Q = (\int) \delta A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where $(\int)$ denotes integration round a cycle.

The notation adopted in (11) expresses the fact that dU is a *perfect* (or *complete*) *differential*, *i.e.*, the change of U depends only on the initial and final states, and is independent of the path. δQ

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[1] *Trans. R. S. Edin.* 1851.

and δA are not perfect differentials, since each depends on the path of change.[1]

Equation (10) shows that an *aschistic change* is a special case of an *isenergic change*, and the latter expression will be used exclusively in what follows.

11. The Compression of a Gas.—As an example of the application of the First Law of Thermodynamics we may consider the compression of a gas.

Let a given quantity of the gas be enclosed in a cylinder in which there is a piston of area a moving without friction. Let the initial state (A) be a volume V_1 at a pressure p_1 at a temperature θ. Now let the gas be compressed to a volume V_2. This change can be carried out in an *infinite* number of ways. Heat will be produced by the compression, and there will be *two* limiting cases in the manner of compression :—

(1) The heat produced is allowed to pass out through the walls of the cylinder to a large water-bath, in which the cylinder is immersed, in such a way that the temperature of the gas remains constant. This is called an *isothermal compression*. Let the final pressure reached by this method be p_θ, and let the final state of the gas be denoted by B (V_2, p_θ).

(2) The heat generated by the compression is completely retained in the gas by the cylinder, which may be assumed to have perfectly non-conducting walls, or else the compression is carried out so rapidly that no appreciable transfer of heat by conduction (which is relatively slow) can occur. This is called an *adiabatic compression*. Let the final pressure be p_Q, and call the state of the gas C (V_2, p_Q). It is an experimental fact that $p_Q > p_\theta$.

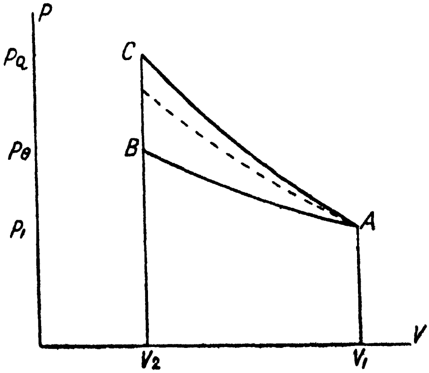

FIG. 4.

If we represent V as abscissa and p as ordinate, the area enclosed between the curve $p = f(V)$, the axis of V, and the two extreme ordinates, is (Fig. 4) $\int_{V_1}^{V_2} pdV$.[1] But, for a small change of volume, dV,

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[1] A proper understanding of thermodynamics requires a knowledge of the properties of *perfect differentials*. The reader is referred to *H. M.*, §§ 57, 115, in which the treatment adopted is that of Clausius, "Die Mechanische Wärmetheorie," 3 vols., 1876; Eng. tr., Browne, 1879.

$$pdV = p \cdot (adx) = (pa) \cdot dx = Pdx,$$

where dx is the (upward) displacement of the piston, and $P = pa$ is the force acting on the piston.[2] But *force* × *displacement along it* = *work* $\therefore pdV = \delta A$.

Thus the area in question, $\int pdV$, is a measure of the work done, or spent, in the change of volume :

$$\int pdV = \Sigma A \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

When dx is an outward displacement, *i.e.*, in the direction of the force, the work is positive (work done), *i.e.*, *in expansion work is done by the system. In compression, work is spent on the system.* In other words, if $dV > 0$, then $\delta A > 0$, whilst if $dV < 0$, then $\delta A < 0$.

The curve representing the various values of p corresponding with the various values of V, will obviously depend on the nature of the compression. Between the two limiting curves, AC for adiabatic, and AB for isothermal, compression, there will be an infinite number of possible compression curves, one of which is represented by a dotted line, these corresponding with different extents to which heat is allowed to escape from the system, and hence there will be an infinite number of expressions for the work. *The work depends entirely on the path of change.*

The heat evolved in the compression will also vary in amount from the maximum in isothermal compression to zero in adiabatic compression. (It must be emphasised that Q denotes the heat absorbed from, or $-$ Q that evolved to, external bodies, by the system. Although heat is generated in the system itself by adiabatic compression, Q is still zero, since no exchange with the environment has occurred.) *The heat evolved depends entirely on the path of change.*

The two final states represented by B and C are different. The gas at C has a higher temperature than that at B. But if the gas at C is cooled at constant volume until its temperature corresponds with B, *i.e.*, the initial temperature, the changes along ACB and

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[1] See below. § 13, also *H. M.*, § 100.
[2] See *H. M.*, § 106.

AB reach the same final state from the same initial state. Hence (11) shows that the changes of intrinsic energy along ACB and AB are equal, *i.e.*, $\Sigma Q - \Sigma A = U_B - U_A$ is constant, where $U_A = f(V_1, \theta)$ and $U_B = f(V_2, \theta)$ are the intrinsic energies in the states A and B respectively.

Since ΔU depends only on the initial and final states, dU is a perfect differential.

Criterion of Euler.

Let $dz = Xdx + Ydy$ $(X = f_1(x,y)\,;\ Y = f_2(x,y))$, then dz is *a perfect* (or *complete*) *differential* when

$$\partial^2 z/\partial x\partial y = \partial^2 z/\partial y\partial x$$

or

$$\partial X/\partial y = \partial Y/\partial x.$$

This will be used in future discussions.[1]

EXAMPLES II.

1. The following figures were found by Joule in one of his water-stirring experiments. The water equivalent of the calorimeter and contents = 6315·97 gms.; the observed rise in temperature on stirring = 0·3196° C., the estimated cooling (from Newton's Law) being equivalent to — 0·0067° C. The fall of the weights, which were equal to 26318·223 gms., was 3201·001 cm., and the drop was repeated 20 times, the mean velocity of fall being 6·15 cm./sec. The elasticity of the string does work 11701·287 gm. cms. each drop. Part of this, however, is spent in producing vibration in the apparatus and in producing sound. The latter portion of this waste of energy Joule determined by measuring the work necessary to obtain from a 'cello a note of the same pitch and intensity. In the case of water, however, we may neglect these two sources of error. Calculate from these figures the value of J, neglecting the resistance offered by the air to the fall of the weights (for which, however, Joule corrected).

2. The following figures were those obtained by Joule in the best experiment on the thermal effects of an electric current in his researches on the value of J. A coil of Pt-Ag wire (doubled on itself to prevent induction) well insulated by a thin coating of shellac and mastic varnish, was immersed in an insulated Cu calorimeter full of water. The current passing through the wire was measured by the deflection produced on a tangent galvanometer, and the rise in temperature of the water was observed on an accurate thermometer:

Water equivalent of calorimeter and contents = 6081·96 gms.
Corrected rise in temperature . . . = 1·312° C.
Time current is passing (t) . . . = 1 hour.
Resistance of coil (R) . . . . = 98953×10^{-5} ohms.
Deflection of galvanometer (θ) . . . = 30° 46′ 15″.
Constant of galvanometer (k) . . . = 3·0426.
Horizontal component of Earth's Field (H) .. = 0·16957 dynes.

Calculate the value of J in ergs; if g = 981·3 cm./sec.² at Manchester, calculate also J in gm. cm. (N.B.—Heating effect of current = C^2Rt; also, for tangent galvanometer, $C = Hk \tan\theta$, where C = current.)

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[1] *H. M.*, § 57.

3. Find the change of intrinsic energy (ΔU) which takes place when 100 grams of water evaporate at 25° C. under a pressure of 750 mm., assuming that water vapour behaves as an ideal gas. Express the result in (*a*) calories, (*b*) ergs.

4. Find the change of intrinsic energy when 20 grams of ethyl alcohol are vaporised at the boiling point, given that L_e is 205 cals. per gram and that the specific volume of the vapour at the boiling point is 607 c.c. per gram. Neglect the specific volume of the liquid.

5. Find the work done in ergs and in gm. cal. when the volume of a system increases by 5 litres under a constant pressure of 1 atm.

6. Assuming the equation $pv = p_0v_0(1 + \theta/273)$ for a gas, where $p, v =$ pressure and volume at temperature θ° C., $p_0, v_0 =$ pressure and volume at 0° C., find an expression for the work of isothermal expansion from a volume v_1 to a volume v_2 at temperature θ. In the case of air, 1 c.c. weighs 0·001293 gm. at $p_0 = 1$ atm., and $\theta = 0$. Find the work in gm. cal. and in gm. cm. when 1 litre of air expands to 10 litres at 17° C.

7. The law of expansion of a gas is $pv^{1\cdot 2} = const.$ Find the work done in gm. cals. when 1 litre at 10 atm. pressure expands to a pressure of 1 atm.

8. Find the energy in ergs given out when 1 kgm. of iron (specific heat 0·1175) cools from 250° to 10° C.

9. The melting point of Zn is 419° C., and its latent heat of fusion is 28 cals. per gm. Find, in ergs, the energy lost by 300 gms. of this metal on cooling from 500° C. to 0° C., the true specific heat being given by the equation (Bède, 1855) $c = 0{\cdot}0865 + 0{\cdot}000064\,\theta$.

10. Joule determined the value of the mechanical equivalent of heat by measuring and equating the work performed on compressing a gas and the resulting heat liberated. Calculate J from the following figures found in an experiment working on these lines: The air was compressed into a Cu reservoir of volume 2237 c.c.; the atmospheric pressure = 771·65 mm. and the initial volume of air compressed = 23,482 c.c. The reservoir was immersed in 1351·07 gms. water, the temperature of which rose 0·981° C. (N.B.—Joule corrected for radiation and for the friction due to the piston working in the pump. Assume ideal gas.)

CHAPTER III

Applications of the First Law of Thermodynamics

12. Specific and Latent Heats.—We can represent du, the increase of intrinsic energy of unit mass of a substance as a function of v and θ :

$$du = (\partial u/\partial \theta)_v d\theta + (\partial u/\partial v)_\theta dv \quad . \quad . \quad . \quad . \quad (14)$$

where $(\partial u/\partial \theta)_v$ is the rate of change of u with θ when v is constant, and $(\partial u/\partial v)_\theta$ the rate of change of u with v when θ is constant. Both, in general, are functions of v and θ.

But $\qquad \delta Q = du + \delta A$; and $\delta A = pdv$

$$\therefore \qquad \delta Q = (\partial u/\partial \theta)_v d\theta + [(\partial u/\partial v)_\theta + p]dv \quad . \quad . \quad . \quad (15)$$

In (15) put $dv = 0$, then :

$$\boldsymbol{c_v \equiv (\partial Q/\partial \theta)_v = (\partial u/\partial \theta)_v} \quad . \quad . \quad . \quad . \quad \mathbf{(16)}$$

since $(\partial Q/\partial \theta)_v$ is the heat absorbed per unit mass per 1° rise in temperature at constant volume, *i.e.*, the specific heat at constant volume, c_v.

If we write (15) in the form :

$$\delta Q = c_v d\theta + [(\partial u/\partial v)_\theta + p]dv \quad . \quad . \quad . \quad . \quad (17)$$

and put $d\theta = 0$, we find :

$$(\partial Q/\partial v)_\theta = (\partial u/\partial v)_\theta + p \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Now $(\partial Q/\partial v)_\theta$ is the heat absorbed per unit increase in volume at constant temperature ; it is a latent heat, and is called the *latent heat of expansion,* denoted by l_v. Hence :

$$(\partial u/\partial v)_\theta = l_v - p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Also from (17) : $\qquad \delta Q = c_v d\theta + l_v dv$

or $\qquad dQ/d\theta = c_v + l_v \, . \, dv/d\theta.$

Now $dQ/d\theta$, which is a specific heat, can have all possible values, depending on all the possible values of $dv/d\theta$ (see § 11). Hence there is an infinite number of specific heats for a substance, depending on the manner of expansion as heat is absorbed.

If the expansion takes place at constant pressure :

$$\boldsymbol{c_p \equiv (\partial Q/\partial \theta)_p = c_v + l_v \, . \, (\partial v/\partial \theta)_p} \quad . \quad . \quad \mathbf{(20)}$$

since $(\partial Q/\partial \theta)_p$ is the amount of heat absorbed per unit mass, for 1° rise in temperature at constant pressure, *i.e.*, the specific heat at constant pressure, c_p. This has a definite value, since $(\partial v/\partial \theta)_p$ has a definite value. The *coefficient of expansion* of the substance is :

$$a = \frac{1}{v_0}\left(\frac{\partial v}{\partial \theta}\right)_p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (21)$$

where v_0 = volume at 0° C.

If the substance is an *ideal gas*, and we take one mol, M, then $Mc_v = C_v, Mc_p = C_p$. Also $pv = RT \quad \therefore \quad v = RT/p$, and $\therefore \quad (\partial v/\partial \theta)_p = R/p$.

Thus, from (20): $C_p = (\partial Q/\partial \theta)_p = C_v + l_v \cdot R/p$.

But $C_p - C_v = R$ (34*a*) $\therefore \quad l_v = p$.

13. **Work done by a Fluid on Change of Volume.**—A fluid is defined as follows :

(1) The pressure exerted by it on a plane area is always at right angles to the area.

(2) The pressure at a point in the fluid is equally great in all directions.

In both cases the fluid is assumed to be at rest.

We see that the work done in expansion depends on these two assumptions.

In all cases the work done in the very small expansion δv of a fluid is given by :

$$A = p\delta v$$

where p is the pressure to which the surface is exposed.[1]

The work done in a finite expansion from volume v_1 to volume v_2 is

$$A = \int_{v_1}^{v_2} p\,dv$$

and is represented graphically as shown in Fig. 5.[2]

If the point representing the state of the gas (*i.e.*, a definite value of v associated with a definite value of p) traces out a closed *loop* and so returns to the initial point, the work done in the *cycle* is positive when the loop is traced out in a clockwise sense, and negative when it is traced out in a counter-clockwise sense.[3] For, in Fig. 6, if the expansion occurs along AαB, and the compression along BβA, then:

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[1] See *H. M.*, § 107.

[2] The p, v diagram is known as the *Indicator Diagram.* It was first used by James Watt, but the applications to thermodynamics were pointed out by Clapeyron in 1834. Cf. § 11 and § 29.

[3] See *H. M.*, § 111.

$$\begin{aligned} &\text{work done in the expansion} = \text{area } \mathrm{A}\alpha\mathrm{B}v_2v_1\,; \\ &\text{work spent in the compression} = \text{area } \mathrm{B}\beta\mathrm{A}v_1v_2\,; \\ \therefore\quad &\text{nett work done} = \text{area } \mathrm{A}\alpha\mathrm{B}v_2v_1 - \text{area } \mathrm{B}\beta\mathrm{A}v_1v_2 \\ &\qquad = \text{area } \mathrm{A}\alpha\mathrm{B}\beta = \text{area of the loop.} \end{aligned}$$

This is positive when the loop is traced out clockwise, since area AαBv_2v_1 is $>$ area BβAv_1v_2. If the loop is traced out counter-clockwise, the larger area is negative, corresponding with a compression, and the nett work is negative. If more than one loop is traced out, the nett work is the algebraic sum of the areas.

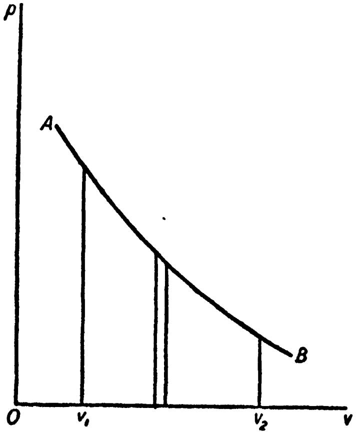

FIG. 5.

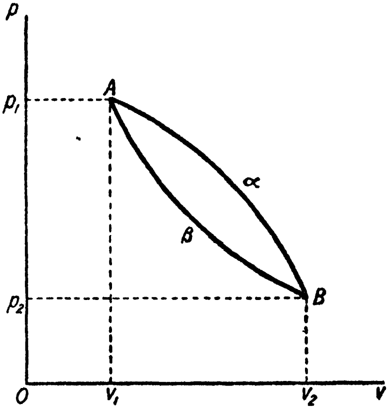

FIG. 6.

The work done in the expansion along AαB may be written down in the form[1]:

$$\mathrm{A} = \int_{v_1}^{v_2} pdv = (p_2v_2 - p_1v_1) - \int_{p_1}^{p_2} vdp \quad . \quad . \quad . \quad (22)$$

In the case of an *ideal gas* undergoing isothermal expansion, $p_1v_1 = p_2v_2$, by Boyles' law,

$$\therefore \qquad \mathrm{A_T} = \int_{v_1}^{v_2} pdv = -\int_{p_1}^{p_2} vdp \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

---

[1] See *H. M.* § 104. If the gas expands suddenly from a pressure p_2 to a pressure p_1 by rushing through a valve, the work done is $p_2v_2 - p_1v_1$, and $-\int_{p_1}^{p_2} vdp$ represents the work lost as compared with expansion in a cylinder.

In other cases the two expressions are different.
For 1 mol $p = \mathrm{RT}/v$:

$$\therefore \quad \mathrm{A_T} = \mathrm{RT}\int_{v_1}^{v_2}\frac{dv}{v} = \mathrm{RT}\ \ln\frac{v_2}{v_1}, \text{ where } \ln = \text{natural logarithm} = \log_e.$$

N.B.—"log" means $\log_{10}$, and $\ln x = 2{\cdot}3026 \log x$.

14. Units of Work.—The unit of work done in expansion depends on the units of p and v. Its dimensions are those of energy, viz., $[ms^2/t^2]$ (§ 6, note).

In C.G.S. units, p is in dynes per cm^2., and v in cm^3.

$$\therefore \quad pv = \frac{[\text{dyne}]}{[\text{cm.}]^2} \times [\text{cm.}]^3 = [\text{dyne}] \times [\text{cm.}] = [\text{erg}].$$

If p is in grams weight per cm^2., and v in cm^3., $pv = [\text{gm. wt.}] \times [\text{cm.}]$.

A convenient unit for gaseous expansion is obtained by measuring p in *standard atmospheres* ($76 \times 13{\cdot}59545 \times 980{\cdot}616 = 1{\cdot}013 \times 10^6$ dynes/cm^2. at sea-level and latitude 45° C.) and v in *litres.* The work done by expansion through 1 litre under a constant pressure of 1 atm. is called a *litre atmosphere* (*l. atm.*). The unit of pressure called the *megabar* is 10^6 dynes per cm^2.

$p = 1$ atm. $= 1013225$ dynes per cm^2. $= 1033{\cdot}2525$ gm. weight per cm^2. at sea-level and latitude 45° C.

$v = 1$ litre $= 1000{\cdot}027$ cm^3.

$\therefore \quad p \times v = 1$ l. atm. $= 1013225 \times 1000{\cdot}027 = 1013{\cdot}25 \times 10^6$ ergs

$= 1033{\cdot}2802 \times 10^3$ gm. cm.

But 1 gm. cal. $= 4{\cdot}184 \times 10^7$ ergs.

$\therefore$ 1 l. atm. $= 24{\cdot}22$ gm. cal.

or 1 gm. cal. $= 0{\cdot}04129$ l. atm.

TABLE SHOWING RELATIONS BETWEEN THE VARIOUS UNITS.

—	Ergs.	Joules.	15° Cal.	Lit. Atm.	Gm. cm.
1 Erg =	1	10^{-7}	$0{\cdot}23901 \times 10^{-7}$	$9{\cdot}8692 \times 10^{-10}$	$1{\cdot}01977 \times 10^{-8}$
1 Joule =	10^7	1	$0{\cdot}23901$	$9{\cdot}8692 \times 10^{-8}$	$1{\cdot}01977 \times 10^4$
1 15° cal. =	$4{\cdot}184 \times 10^7$	$4{\cdot}184$	1	$4{\cdot}129 \times 10^{-2}$	$4{\cdot}2667 \times 10^4$
1 lit. atm. =	$1{\cdot}01325 \times 10^9$	$101{\cdot}325$	$24{\cdot}22$	1	$1{\cdot}0333 \times 10^6$
1 gm. cm. =	$9{\cdot}80616 \times 10^2$	$9{\cdot}80616 \times 10^{-5}$	$2{\cdot}3437 \times 10^{-5}$	$9{\cdot}6777 \times 10^{-7}$	1

15. Thermal Coefficients.—A fluid of invariable chemical composition (gas, liquid, and in many cases solid) is completely defined as to its state by the values of any *two* of the variables: v = *specific volume* (volume of unit mass; or, alternatively, ρ the density, or mass of unit volume), p = pressure; θ = temperature, provided that the effects of electrification, magnetisation, internal stress, and surface tension are negligible, as is usually the case.

The *state* of the fluid can thus be represented by the equation :

$$f(p, v, \theta) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Thus, the state of an ideal gas is defined by :

$$pv - \mathrm{RT/M} = 0$$

where R is the gas-constant and M the molar weight.

The state of a fluid obeying Van der Waals' equation is defined by :

$$\left(p + \frac{a}{v^2}\right)(v - b) - \frac{\mathrm{R}}{\mathrm{M}}\mathrm{T} = 0.$$

Equation (24) is called the *characteristic equation,* or the *equation of state,* of the fluid.

If a small change of state (dv, dp, $d\theta$) occurs, the small amount of heat absorbed per unit mass may be represented by any one of the three equations :

$$\left.\begin{aligned} \delta \mathrm{Q} &= c_v d\theta + l_v dv \\ &= c_p d\theta + l_p dp \\ &= \gamma_v dv + \gamma_p dp \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

In these, c_v and c_p are the *specific heats* at constant volume and at constant pressure ; l_v and l_p are the *latent heats* of volume change and pressure change ; and γ_v and γ_p are coefficients which have received no special names.

These six magnitudes, which are not necessarily constants, are known as the *thermal coefficients* of the fluid. Their physical meanings are defined by the equations when one differential is equated to zero :

E.g., in $\delta\mathrm{Q} = c_v d\theta + l_v dv$ put $d\theta = 0$

$\therefore \quad (d\mathrm{Q}/dv)_\theta = l_v =$ amount of heat absorbed per unit increase in volume at constant temperature, per unit mass.

16. Theorem of Reech : Ratio of Specific Heats.—Consider an *isothermal change* of the fluid :

$$\begin{aligned} d\theta = 0 \quad \therefore \quad (\delta\mathrm{Q})_\theta &= l_p dp \quad \therefore \quad dp = (\delta\mathrm{Q})_\theta / l_p \\ (\delta\mathrm{Q})_\theta &= l_v dv \quad \therefore \quad dv = (\delta\mathrm{Q})_\theta / l_v \end{aligned} \qquad \therefore \left(\frac{\partial p}{\partial v}\right)_\theta = \frac{l_v}{l_p}$$

Consider an *adiabatic change :*

$$\begin{aligned} \delta\mathrm{Q} = 0 \quad \therefore \quad c_p d\theta + l_p dp &= 0 \quad \therefore \quad dp = -\frac{c_p}{l_p} d\theta \\ c_v d\theta + l_v dv &= 0 \quad \therefore \quad dv = -\frac{c_v}{l_v} d\theta \end{aligned} \qquad \therefore \left(\frac{\partial p}{\partial v}\right)_\mathrm{Q} = \frac{c_p l_v}{c_v l_p}$$

Thus : $$(\partial p/\partial v)_\mathrm{Q} / (\partial p/\partial v)_\theta = c_p/c_v = \gamma \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

This is known as *Reech's theorem* (1854); it is perfectly general and does not involve either law of thermodynamics.[1]

17. Elasticity and Compressibility.—The coefficient of elasticity, ϵ, of a fluid is defined as the limiting value of:

(small increase of pressure)/(resulting fractional decrease in volume).

Let δp be the *in*crease of pressure, δv the *in*crease in volume, v_0 the initial volume, *e.g.*, the specific volume, then:

$$\epsilon = \lim_{\delta v \to 0} - \delta p/(\delta v/v_0) = - v_0 \frac{dp}{dv} \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The value of ϵ will depend on that of dp/dv, *i.e.*, on the conditions under which the compression is executed. δv and δp have opposite signs in stable states (cf. § 46), hence ϵ is positive. The reciprocal of the elasticity:

$$\eta = - 1/v_0 \, . \, dv/dp \quad . \quad . \quad . \quad . \quad . \quad (27a)$$

is the *coefficient of compressibility*.[2]

There are two important special values of ϵ, according as the compression is carried out *isothermally* (ϵ_θ), or *adiabatically* (ϵ_Q). Then:

$$\epsilon_Q/\epsilon_\theta = (\partial p/\partial v)_Q \,/\, (\partial p/\partial v)_\theta$$

and hence, by Reech's theorem:

$$\boldsymbol{\epsilon_Q/\epsilon_\theta = c_p/c_v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \mathbf{(28)}$$

i.e., the ratio of the specific heats at constant pressure and at constant volume is equal to the ratio of the adiabatic and isothermal elasticities.

18. Relations between Thermal Coefficients.—Consider the two sets of equations:

$$\begin{aligned} \text{I.}\quad \delta Q &= c_v d\theta + l_v dv && (a) \\ &= c_p d\theta + l_p dp && (b) \\ &= \gamma_v dv + \gamma_p dp && (c). \end{aligned}$$

$$\begin{aligned} \text{II.}\quad d\theta &= (\partial\theta/\partial p)_v dp + (\partial\theta/\partial v)_p dv && (a) \\ dv &= (\partial v/\partial\theta)_p d\theta + (\partial v/\partial p)_\theta dp && (b) \\ dp &= (\partial p/\partial v)_\theta dv + (\partial p/\partial\theta)_v d\theta && (c). \end{aligned}$$

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[1] See Duhem, *C. R.*, 1906, **143**, 371, for extension.

[2] Table of compressibility coefficients in Jellinek, "Phys. Chem.," I., 511; Landolt-Börnstein, 4th ed., 58 ff.; Richards and others, numerous papers in *J. A. C. S.* to date. Also Bridgman, *Proc. Amer. Acad. Arts and Sci.*, 1923, **58**, 166.

In II.*a*, put $d\theta = 0$ (isothermal change):

$$\therefore \quad (\partial\theta/\partial v)_p dv + (\partial\theta/\partial p)_v dp = 0$$

$$\left.\begin{aligned} &\therefore & \left(\frac{\partial p}{\partial v}\right)_\theta &= -\frac{(\partial\theta/\partial v)_p}{(\partial\theta/\partial p)_v} \\ &\text{Similarly} & \left(\frac{\partial p}{\partial \theta}\right)_v &= -\frac{(\partial v/\partial\theta)_p}{(\partial v/\partial p)_\theta} \\ &\text{and} & \left(\frac{\partial v}{\partial \theta}\right)_p &= -\frac{(\partial p/\partial\theta)_v}{(\partial p/\partial v)_\theta} \end{aligned}\right\} \quad \ldots\ldots \quad (29)$$

In II.*a*, put $dp = 0$ (isopiestic change):

$$\left.\begin{aligned} &\therefore & (\partial v/\partial\theta)_p &= 1/(\partial\theta/\partial v)_p \\ &\text{Similarly} & (\partial v/\partial p)_\theta &= 1/(\partial p/\partial v)_\theta \\ &\text{and} & (\partial\theta/\partial p)_v &= 1/(\partial p/\partial\theta)_v \end{aligned}\right\} \quad \ldots\ldots \quad (30)$$

Relations II., (29) and (30) are quite general and hold for *any* three variables $f(p, v, \theta) = 0$.

If we fix the values of the two differentials in any *one* of equations I., those in the other two equations are fixed, since there are only two independent variables. From the above set of equations we readily find a number of relations between the thermal coefficients, such as:

$$c_v = c_p + l_p(\partial p/\partial\theta)_v \quad \ldots\ldots \quad (31)$$

$$l_v = l_p(\partial p/\partial v)_\theta \quad \ldots\ldots \quad (32)$$

They are all purely mathematical and independent of thermodynamics.

19. Difference of Specific Heats.—For change of unit mass of a fluid at constant pressure, we find from (15):

$$\boldsymbol{c_p - c_v = [p + (\partial u/\partial v)_\theta](\partial v/\partial \theta)_p} \quad . \ . \quad \mathbf{(33)}$$

The term $p(\partial v/\partial\theta)_p$ represents the external work done per 1° rise in temperature; the term $(\partial u/\partial v)_\theta \,.\, (\partial v/\partial\theta)_p$ represents the increase in intrinsic energy per 1° rise in temperature at constant pressure. In the case of liquids and solids the first term is usually negligible in comparison with the second; in the case of gases the second term is usually very small in comparison with the first.

In the case of an *ideal gas* we shall assume (§ 33) that $(\partial u/\partial v)_\theta = 0$:

$$\begin{aligned} \therefore c_p - c_v &= p\,(\partial v/\partial\theta)_p \quad \ldots\ldots \quad [34] \\ &= (\text{pressure}) \times (\text{increase in volume per } 1^\circ \text{ rise in temperature at constant pressure}) \\ &= \text{work of expansion per } 1^\circ \text{ rise in temperature.} \end{aligned}$$

Now $pv = \mathrm{RT/M} \quad \therefore \quad p(\partial v/\partial \theta)_p = \mathrm{R/M}$,

or $$\mathrm{C}_p - \mathrm{C}_v = \mathrm{R} = 1{\cdot}987 \text{ gm. cal. per mol} \quad . \quad . \quad . \quad [34a]$$

It is important to notice that *this result applies only to ideal gases.* In the case of air the value of $\mathrm{C}_p - \mathrm{C}_v$ is 1·993 at 17°, and in the case of carbon dioxide at the same temperature it is 2·038.[1] In the second case the difference from the ideal value, 1·987, amounts to about 2·5 per cent.

It is evident that if c_p and c_v (or c_p/c_v) and $(\partial u/\partial v)_\theta$ are known for a substance, the application of equation (33) will give a value of the mechanical equivalent of heat, but $(\partial u/\partial v)_\theta$ is hardly known for the majority of substances.

In the case of air $c_p = 0{\cdot}2389$ cal.,[2] $c_p/c_v = 1{\cdot}403$,[1] $\therefore c_v = 0{\cdot}1702$, $\therefore c_p - c_v = 0{\cdot}0687$ cal.

If we *assume* that this difference is entirely spent in doing work against the atmospheric pressure, *i.e.*, $(\partial u/\partial v)_\theta = 0$, then

$$(c_p - c_v) \times \mathrm{J} = \text{pressure} \times \text{increase of volume.}$$

The volume of 1 gm. of air at 0° C. = 773·4 c.c., and the increase in volume per 1° is very nearly 1/273 of the volume at 0°, hence the expansion is 773·4/273 = 2·83 c.c. Also, 1 atm. = 1033 gm. per cm^2.

$$\therefore \text{ external work} = 1033 \times 2{\cdot}83 = 2923{\cdot}4 \text{ gm. cm.}$$

Thus 1 gm. cal. = 2923·4/0·0686 = 42,615 gm. cm. = J, which is in fair agreement with the value directly determined, 42,670 (§ 6).

The assumption $(\partial u/\partial v)_\theta = 0$ tacitly introduced by Mayer[3] was called into question by Joule in 1845, who showed by experiment (§ 33) that it is very approximately true for air. Mayer's calculation was, by chance, very nearly right, but he can hardly be credited with the first *determination* of the mechanical equivalent of heat.

20. Enthalpy ; Total Heat ; Heat Function.—In any change of a system : the *heat absorbed at constant volume :*

$$\mathrm{Q}_v = \mathrm{U}_2 - \mathrm{U}_1 = \text{increase of intrinsic energy ;}$$

the *heat absorbed at constant pressure :*

$$\begin{aligned}\mathrm{Q}_p &= (\mathrm{U}_2 - \mathrm{U}_1) + \mathrm{A} = (\mathrm{U}_2 - \mathrm{U}_1) + p(\mathrm{V}_2 - \mathrm{V}_1) \\ &= (\mathrm{U}_2 + p\mathrm{V}_2) - (\mathrm{U}_1 + p\mathrm{V}_1) \\ &= \mathrm{H}_2 - \mathrm{H}_1\end{aligned}$$

where $$\mathbf{H} = \mathbf{U} + p\mathbf{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

The heat absorbed at constant volume is the increase of U, that at constant pressure the increase of H.

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[1] J. R. Partington, *P. R. S.*, 1921, **100**, *A*, 27.

[2] E. Wiedemann, *A. P.*, 1876, **157**, 1; the value deduced from c_p/c_v by means of Berthelot's equation (§ 37) is 0·2391 gm. cal.

[3] The statement that Mayer defended the assumption by reference to an experiment made by Gay Lussac (Bertrand, "Thermodynamique," Paris, 1887, p. 66) is incorrect. There is no mention of such experiments in Mayer's original communication, and he does not even point out that he is making any assumption. The quotation given by Bertrand is given in Mayer's paper issued in 1845, after the publication of the work of Joule, who is not mentioned.

Q is independent of the path of absorption at constant volume; at constant pressure the path is fixed. $dQ_v = dU$, and $dQ_p = dH$ are therefore perfect differentials. The function H was called by Gibbs the *heat function at constant pressure*, and denoted by χ; the name *enthalpy* has been proposed by Kamerlingh Onnes[1] (τό θαλπος = *heat*). It is usually called by engineers the *total heat*, or *heat content*, but these names refer to an obsolete period in the theory of heat.

By differentiation:

$$(\partial H/\partial T)_p = (\partial Q_p/\partial T)_p = c_p \quad . \; . \; . \; . \; . \; . \; . \qquad . \; (36)$$

$$(\partial H/\partial p)_T = (\partial U/\partial p)_T + v + p\,(\partial v/\partial p)_T = l_p + v \quad . \; (36a)$$

since $dU + pdv = \delta Q$ (see (25) and § 19).

EXAMPLES III.

1. The coefficient of expansion of alcohol is $0{\cdot}0_5110$. Find the external work done (in ergs) when 1 litre of alcohol is heated from 0° to 25° C. under 1 atm. pressure.

2. The coefficient of cubical expansion of copper is $50{\cdot}1 \times 10^{-6}$. Find the ratio of the external work done to the heat absorbed when a kilogram of copper (density 8·93; specific heat 0·0936) is heated from 0° to 250° C. at 1 atm. pressure.

3. The specific heats of CO_2 are $c_p = 0{\cdot}1996$ and $c_v = 0{\cdot}1531$ at 17° C.; the coefficient of expansion is 0·00372 and the density at 0° C. is 0·0019768 gm./c.c. Find $(\partial u/\partial v)_\theta$ at 17° C. Assuming this constant, find the heat absorbed when 1 litre of CO_2 at 17° C. expands to 11 litres without external work.

4. Show that: $c_v = \gamma_p(\partial p/\partial \theta)_v$: $l_p = \gamma_p + \gamma_v\,(\partial v/\partial p)_\theta$; $l_p/\gamma_p = -(c_p - c_v)/c_v$. The value of c_v for air is 0·1704, and $p_\theta = p_0(1 + 0{\cdot}00367\,\theta)$; find the value of γ_p at 1 atm. pressure in gm. cal. per atm.

5. Show that: $\gamma_v = c_p(\partial \theta/\partial v)_p$. The value of c_p for air is 0·2391; the coefficient of expansion is 0·003673; find the value of γ_v at 0° and 1 atm.

6. The adiabatic compressibility of benzene at 20° C. is $66{\cdot}25 \times 10^{-6}$ atm.$^{-1}$, the isothermal value being $95{\cdot}3 \times 10^{-6}$. The specific heat c_p (1 atm.) is 0·4084. Find c_v.

7. Find the isothermal elasticity of a fluid $(p + a/v^2)\,(v - b) = k$, where a, b, k are constants.

8. The following isothermal compressibilities in megabar^{-1} (1 megabar $= 10^6$ dynes per sq. cm.) are given by Richards[2]: mercury $3{\cdot}71 \times 10^{-6}$; CCl_4 $89{\cdot}6 \times 10^{-6}$. Find the decrease in volume of 1 litre of each liquid when the pressure is raised from 1 to 100 atm.

9. The coefficient of expansion of benzene is $0{\cdot}0_5124$; the density at 20° C. is 0·879. Assuming the result of Ex. 6, find $(\partial u/\partial v)_\theta$ in gm. cal. per c.c. per gram of benzene.

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[1] See Porter, *F. S.*, 1922, **18**, 140; it is usually denoted in engineering treatises by H, which (as Greek *eta*) may also stand for enthalpy.

[2] *Z. p. C.*, 1907, **61**, 171.

10. The value of c_p for hydrogen is 3·40. Assume an ideal gas and find the value of c_v.

11. Show that $c_p - c_v = [v - (\partial H/\partial p)_T](\partial p/\partial T)_v$. Find $(\partial H/\partial p)_T$ at 17° in gm. cal. per atm. per gm., for CO_2, using the data of Ex. 3 and the value $\beta = (1/p_0) . (\partial p/\partial T)_v = 0{\cdot}00373$.

12. One mol of hydrogen is heated from 0° to 100° C. at 1 atm. pressure; find the increase in enthalpy. Assuming a perfect gas, find the increase in intrinsic energy. (c_p for $H_2 = 3{\cdot}70$.)

CHAPTER IV

Thermochemistry

21. **Thermochemistry.**—The two equations

$$U_2 - U_1 = Q_v \ (v \text{ const.})$$
$$H_2 - H_1 = Q_p \ (p \text{ const.})$$

are fundamental in thermochemistry. In the study of heats of reaction, however, it is usual to take *heat evolved as positive.* We shall then write $\boldsymbol{Q}_v = - Q_v$ and $\boldsymbol{Q}_p = - Q_p$, when

$$U_1 - U_2 = \boldsymbol{Q}_v\text{; and } H_1 - H_2 = \boldsymbol{Q}_p \quad . \quad . \quad . \quad (37)$$

Now dU and dH are perfect differentials, hence the heat evolved in a chemical change is independent of the intermediate stages and depends only on the initial and final states when : (i.) the volume is constant ($\boldsymbol{Q} = U_1 - U_2$) or (ii.) when the pressure is constant ($\boldsymbol{Q} = H_1 - H_2$). This is *Hess's Law,* which is true only when one or other of the two conditions $v = const.$ or $p = const.$ is fulfilled. The applications of Hess's Law are fully considered in elementary text-books of physical chemistry. In reactions between solids and liquids $\boldsymbol{Q}_p$ is so nearly equal to $\boldsymbol{Q}_v$ that no special conditions need be assumed.

22. **Kirchhoff's Equation.**—It is an experimental fact that the heat of reaction depends on the temperature. The extent of dependence may be calculated as follows :

(1) Let the *initial* material system I be heated at constant volume, or constant pressure, from the temperature θ to the temperature $\theta + d\theta$. The heat absorbed will be $\Gamma_i d\theta$ where Γ_i is the *heat capacity* of the initial system at constant volume or at constant pressure. Now let the system I be changed to the material system F, the *final* system, at the temperature $\theta + d\theta$. Let the heat evolved be $(\boldsymbol{Q}_\theta + d\boldsymbol{Q}_\theta)$, where $\boldsymbol{Q}_\theta$ is the heat of reaction at θ. The total evolution of heat is $-\Gamma_i d\theta + (\boldsymbol{Q}_\theta + d\boldsymbol{Q}_\theta)$.

(2) Let the system I be converted into the system F at the temperature θ. The heat evolved is $\boldsymbol{Q}_\theta$. Now let the system F be heated to $\theta + d\theta$ at constant volume or pressure. The heat

absorbed is $\Gamma_f d\theta$ where Γ_f is the heat capacity of the final system. The total evolution of heat is $-\Gamma_f d\theta + Q_\theta$.

The two amounts of heat are equal by Hess's Law, hence :

$$-\Gamma_i d\theta + (Q_\theta + dQ_\theta) = -\Gamma_f d\theta + Q_\theta$$

or

$$\frac{dQ_\theta}{d\theta} = \Gamma_i - \Gamma_f \quad . \; . \; . \; . \; . \; . \quad (38)$$

We note that Q_θ may be Q_v or Q_p. If it is Q_v we can put $Q_v = -\Delta U = U_1 - U_2$, hence

$$\frac{d\Delta U}{d\theta} = (\Gamma_f - \Gamma_i)_v \quad . \; . \; . \; . \; . \quad (38a)$$

This is *Kirchhoff's Equation.*[1] If Q_p is concerned

$$\frac{dQ_p}{d\theta} = (\Gamma_f - \Gamma_i)_p \quad . \; . \; . \; . \; . \quad (38b)$$

The heat capacities Γ_i and Γ_f are usually functions of temperature. In the *initial system* we have :

$$\Gamma_i = \Sigma n_i C_i$$

where n_i = no. of mols of substance i, and C_i = molecular heat of substance i. According as the reaction occurs at constant volume or pressure we must take c_v or c_p, both TRUE specific heats at the temperature θ : $C_v = Mc_v$, $C_p = Mc_p$.

For the *final system* we have, similarly :

$$\Gamma_f = \Sigma n_f C_f$$

thence :

$$\frac{dQ}{d\theta} = \Sigma n_i C_i - \Sigma n_f C_f \quad . \; . \; . \; . \; . \; . \quad (39)$$

or

$$\frac{d\Delta U}{d\theta} = \Sigma n_f C_{v(f)} - \Sigma n_i C_{v(i)} \quad . \; . \; . \quad (39a)$$

In general $\quad C_i = f_i(\theta)$, and $C_f = f_f(\theta) \quad . \; . \; . \; . \; . \; . \quad (40)$

and in some cases it may even be necessary to consider the effect of pressure as well as temperature on the specific heats.

The above equations enable us to calculate the heat of reaction at any temperature when the heat of reaction at *one* temperature and the specific heats of all the substances involved at all temperatures in the range considered are known. By integration of (38) we have:

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[1] G. Kirchhoff, *A. P.*, 1858, **103**, 177; Ges. Abh., 1882, p. 454.

$$Q_{\theta_2} = Q_{\theta_1} + \int_{\theta_1}^{\theta_2} (\Gamma_i - \Gamma_f)d\theta \quad . \quad . \quad . \quad . \quad . \quad (41)$$

$$Q_\theta = Q_0 + \int_{0}^{\theta} (\Gamma_i - \Gamma_f)d\theta \quad . \quad . \quad . \quad . \quad . \quad (41a)$$

Example.—The heat of formation of steam at constant volume:

$$H_2 + \tfrac{1}{2}O_2 = H_2O \text{ (gaseous).}$$

Initial System.

$C_v(H_2)$[1] $= 4{\cdot}650 + 0{\cdot}75 \times 10^{-3}T$

$C_v(O_2)$[1] (assumed $= N_2$):

$= 4{\cdot}850 + 0{\cdot}75 \,.\, 10^{-3}T$

$\therefore \Gamma_i = C_v(H_2) + \tfrac{1}{2}C_v(O_2)$

$= 7{\cdot}075 + 1{\cdot}125 \,.\, 10^{-3}T$

Final System.

$C_v(H_2O)$[1] $= 5{\cdot}750 + 1{\cdot}566 \,.\, 10^{-3}T - 0{\cdot}1878 \,.\, 10^{-5}T^2 + 0{\cdot}1824 \,.\, 10^{-8}T^3 - 0{\cdot}1308 \,.\, 10^{-15}T^5$

$= \Gamma_f$

Thus $\Gamma_i - \Gamma_f = 1{\cdot}325 - 0{\cdot}441 \,.\, 10^{-3}T + 0{\cdot}1878 \,.\, 10^{-5}T^2 - 0{\cdot}1824 \,.\, 10^{-8}T^3 + 0{\cdot}1308 \,.\, 10^{-15}T^5$
$= dQ_v/d\theta.$

By integration:

$$Q_v = Q_v^0 + 1{\cdot}325T - 0{\cdot}2205 \,.\, 10^{-3}T^2 + 0{\cdot}626 \,.\, 10^{-6}T^3 - 0{\cdot}456 \,.\, 10^{-9}T^4 + 0{\cdot}218 \,.\, 10^{-16}T^6$$

where Q_v^0 = heat of reaction at 0° K. (The above are all absolute temperatures.)

According to Pier,[2] Q_v for steam at 290° K. is 57,290 cal.

$$\therefore \; 57{,}290 = Q_v^0 + 385{\cdot}6 - 18{\cdot}67 + 15{\cdot}43 - 3\ 27 \text{ or } Q_0 = 56{,}911 \text{ cal.}$$

(The remaining terms are negligible at 290° K.)

Thus $Q_v = 56{,}911 + 1{\cdot}325T - 0{\cdot}2205 \,.\, 10^{-3}T^2 + 0{\cdot}626 \,.\, 10^{-6}T^3 - 0{\cdot}456 \,.\, 10^{-9}T^4 + 0{\cdot}218 \,.\, 10^{-16}T^6$.

This is a complete solution of the problem of finding the heat of formation of steam at constant volume at *any* temperature from its value at one temperature, provided the values of c are known over the range of temperatures.

If *solids* or *liquids* take part in the reaction we must, of course, include their heat capacities in Γ_i and Γ_f.

If we are considering *ideal gases* (p const.) we can put:

$$Q_p = Q_v + A = Q_v + p(V_2 - V_1) = Q_v + (n_2 - n_1)RT \quad . \; [42]$$

where n_1 and n_2 are the numbers of mols of gas in the initial and final systems. If Q is in gm. calories, $R = 1{\cdot}987$, or 2 with sufficient approximation.

The heat of reaction is independent of temperature only when $\Gamma_f = \Gamma_i$. This is *approximately* the case in reactions between solids, since according to Joule[1] the molecular heat of a solid is additively composed of the atomic heats of its constituents. The value of Γ then remains constant when the redistribution of atoms occurs in a chemical change.

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[1] Siegel, *Z. p. C.*, 1914, **87**, 653.

[2] *Z. E.*, 1909, **15**, 539.

EXAMPLES IV.

1. The heat of formation of liquid water from its elements ($2H_2+O_2 = 2H_2O$) is 137,000 cals. If the molar heat of evaporation of water, λ_e, is 9,500 gm. cals., calculate the heat of formation of steam from its elements.

2. If the molecular heat at constant pressure of HBr is $6{\cdot}5 + 0{\cdot}0017T$, of Br_2 (gas) $6{\cdot}5 + 0{\cdot}0064T$ and of H_2, $6{\cdot}5 + 0{\cdot}001T$, find an expression for the heat of formation at any temperature of 2HBr from its elements.

If the heat of formation at 320° C. is 12,100 cals. per mol HBr, find the heat of formation of 1 mol at 727° C.

3. The heats of formation of CO and H_2O (gas) at 17° C. are 29 kg. cal. and 58 kg. cal. Find the heat of the reaction (at constant pressure): $C + H_2O = CO + H_2$ at 1000° K., assuming the following true molecular heats at constant pressure: Carbon, $1{\cdot}1 + 0{\cdot}0_248T - 0{\cdot}0_512T^2$; H_2O, $8{\cdot}81 - 0{\cdot}0_219T + 0{\cdot}0_5222T^2$; CO, $6{\cdot}50 + 0{\cdot}001T$; H^2, $6{\cdot}50 + 0{\cdot}0_39T$.

4. The heat of formation of CO_2 from CO and $\frac{1}{2}O_2$ at 273° K. being 68,000 cals., and the true molecular heats as follows:

$$C_V = 5{\cdot}106 + 0{\cdot}00334T - 7{\cdot}35 \times 10^{-7}T^2\,(CO_2)$$
$$C_V = 4{\cdot}68 + 0{\cdot}000268T(CO \text{ and } O_2),$$

what is the heat of formation of $2CO_2$ at 0° K. ?

Find a formula for the heat of reaction at any temperature, and find Q at $T = 1000°$ K.

5. The heat of formation of CO_2 at constant pressure at 15° C. is 68,000 gm. cal. Assuming an ideal gas, find Q_V. Assuming the data in No. 3, taking C_p for O_2, the same as for CO, and C_p for CO_2 as $7{\cdot}0 + 0{\cdot}0_271T - 0{\cdot}0_5186T^2$, and all the gases ideal, find Q_V as a function of T and calculate its value at 1000° C.

6. Given the heats of reaction: $CO + \frac{1}{2}O_2 = CO_2 + 68$ kg. cal., and $H_2 + \frac{1}{2}O_2 = H_2O$ (gas) + 58 kg. cal., at 17° C., and assuming the values of C_V for H_2O as $5{\cdot}78 + 0{\cdot}0_2286\,\theta$ and for CO_2 as $6{\cdot}5 + 0{\cdot}0_2387\,\theta$ (Mallard and Le Chatelier), find a formula for the heat of the reaction $CO + H_2O = CO_2 + H_2$, and calculate the values at 800° C. and 1200° C.

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[1] *P. M.*, 1844, **25**, 334; usually known as "Woestyn's law" (1848).

CHAPTER V

The Second Law of Thermodynamics

23. Transformation of Heat into Work.—The definition of energy implies that all the forms of energy are interconvertible. A quantity of any other form of energy can be completely converted into heat, but it is found that the conversion of heat into any other equivalent form of energy is in general either impossible or only partly possible, unless other changes occur as well. The conversion of heat into work, where " work " means any form of energy other than heat, is restricted by certain conditions, which points to an essential difference between heat and other forms of energy. The *restrictions* are twofold :

1. Those depending only on the *particular manner in which a given process is carried out,* and removable by alteration of this without changing the essential features of the process.
2. Those *inherent in the process itself* and not controllable by any means in our power.

A process which can be performed backwards so that all changes occurring in any part of the direct process are *exactly* reversed in the corresponding part of the reverse process, and no other changes are left in external bodies, is called a *reversible process* in the thermodynamic sense. (A very special type of reversibility.)

Each class of restriction referred to may be shown to involve a corresponding type of *irreversibility.*

Some changes cannot in any actual circumstances be reversed in the thermodynamic sense (Restriction 2). Such are :

(1) Production of heat by friction. (2) Passage of heat from one body to another at a lower temperature by conduction or radiation. (3) The spontaneous mixing or diffusion of matter of different kinds, *e.g.*, the mixing of red and black ink, or of gases. Such changes are called *intrinsically irreversible.*

Other changes may become reversible in the limit with suitable arrangement of conditions (Restriction 1). Such are called *conditionally irreversible.* As an example we may consider the *expansion of a gas.* This becomes reversible when : (i.) the pressure, p, of the gas differs only infinitesimally from that on the frictionless piston, so that a change $\pm\ \delta p$ will send the piston up or down ; (ii.) the temperature of the gas differs only infinitesimally from that of the thermostat, so that a change $\pm\ \delta\text{T}$ will change an absorption into an emission of heat (Fig. 7). Under these ideal conditions the changes of volume occur reversibly, but then infinitely slowly : the system is in *equilibrium. Equilibrium is a state which is independent of time. A reversible change is a continuous succession of equilibrium states :* it is an *ideal* change. If we have a finite pressure difference, rapid motions are set up and heat is produced by fluid friction. If the temperature differences are finite, heat passes from the warmer to the cooler body by conduction or radiation. Both these are intrinsically irreversible changes. Friction of the piston would also lead to irreversible conversion of work into heat.

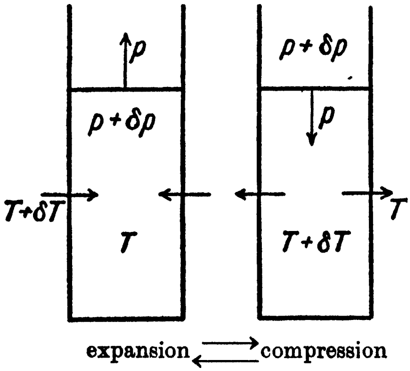

FIG. 7.

24. Reversible Transformation of Heat into Work.—In order that the *reversible transformation of heat*[1] *into work* shall be possible :

1. *All* bodies concerned in the transformation must be left in the same state as they were in at the start, otherwise the process will not be reversible in the thermodynamic sense.
2. If transfer of heat occurs between bodies, their temperatures must differ only infinitesimally, *i.e.*, the transfer must be *isothermal.*
3. If a body is to be brought successively in contact with other bodies at different temperatures, its temperature must be brought to equality with these by adiabatic compression or expansion before contact.

Any arrangement which converts heat into work is called a *heat engine ;* the conditions for its reversibility follow :

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[1] The essential difference between heat and other forms of energy, which is generally overlooked, was clearly expressed by Gibbs (" Scientific Papers," I., 406) : " I use the term ' equivalent ' *strictly* to denote reciprocal convertibility, and not in the loose and often misleading sense in which we speak of heat and work as equivalent when there is only a one-sided convertibility."

(1) It must work in *cycles.* (2) Heat must be exchanged *isothermally* between heat reservoirs and the working substance of the engine. (3) Changes in temperature of the working substance must be achieved *adiabatically.* We assume equality of inside and outside pressures and absence of friction.

25. **Carnot's Cycle.**—Sadi Carnot, in 1824, first studied, in a perfectly general manner, the reversible conversion of heat into work.[1] The result is independent of the particular type of process used, provided all the processes satisfy two conditions :—

1. They must be *cyclic.* 2. They must be *reversible.*

Carnot's cycle comprises *four operations ;* two isothermal and two adiabatic.

Let there be given a *source* of heat (" hot body ") at a temperature T_1, and a *refrigerator* (" cold body ") at a temperature T_2, where $T_1 > T_2$.[2] In order that finite quantities of heat may be added to or taken from these without changes of their temperatures, we may suppose them to consist of *large* reservoirs of water, or, better still, reservoirs of steam and of ice, which would preserve constant temperatures during withdrawal or addition of heat.

Nothing is assumed about the temperatures, and one result of Carnot's investigations is a *definition of temperature* which depends only on the properties of heat, and is independent of the behaviour of particular thermometric substances, such as mercury, or a gas, in terms of the expansion of which temperature scales are usually defined.

Further, let there be given a cylinder and piston, absolute non-conductors of heat, closed at the bottom by a perfect conductor of heat, and containing the working substance, which for simplicity may be supposed to be a gas, although no restrictions are placed upon it. Finally, there is provided a stand for the cylinder, composed of a perfect non-conductor of heat (Fig. 8).

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[1] " Réflexions sur la puissance motrice du feu et sur les moyens propres à développer cette puissance " (Paris, 1824; first edition exceedingly scarce; English translation by R. H. Thurston, 1890). Carnot's notebooks show that he was convinced that the caloric theory of heat (assumed in the memoir) was incorrect, and he surmised that: " Heat is simply motive power, or rather motion which has changed form. Whenever there is destruction of motive power, there is at the same time production of heat in quantity proportional to the quantity of motive power destroyed. Reciprocally, whenever there is destruction of heat, there is production of motive power . . . motive power is in quantity invariable in nature—that is, correctly speaking, never either produced or destroyed." This passage is reproduced in facsimile of Carnot's own writing opposite page 91 of the edition of the " Réflexions," Paris, Gauthier-Villars, 1878, and is printed on page 94. Before his death in 1832, therefore, Carnot had arrived at *both* the fundamental laws of thermodynamics.

[2] We use T_1, T_2 for the temperatures instead of θ_1, θ_2, since we shall later on adopt the former notation. This is not necessary, since nothing is assumed in the present discussion as to the particular scale of temperature adopted—an important circumstance.

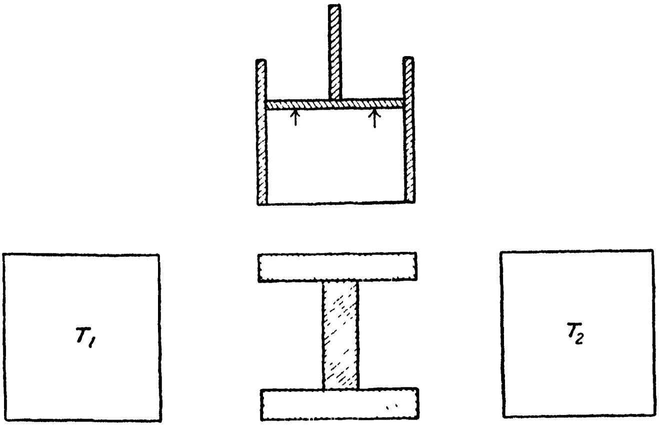

FIG. 8.

The piston is assumed to move without friction, and all the changes are carried out reversibly.

(1) The working substance at the temperature T_2 is compressed adiabatically, by placing the cylinder on the non-conducting stand, until its temperature rises to T_1. The compression is represented on the p, v diagram by the adiabatic curve AB (Fig. 9), the point A representing the substance in its initial state. (In Carnot's original description, the cycle commenced at C.)

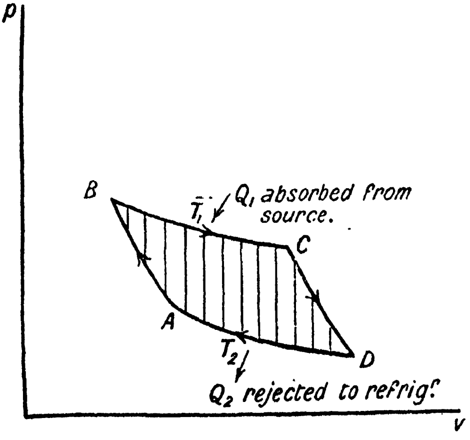

FIG. 9.

(2) The cylinder is placed on the source and the substance allowed to expand isothermally at T_1 until any arbitrary quantity of heat, Q_1, has been absorbed. This step is represented by the isothermal curve BC.

(3) The cylinder is transferred to the stand, and the working

substance allowed to expand adiabatically until its temperature falls to T_2. The expansion is represented by the adiabatic curve CD.

(4) The cylinder is placed on the refrigerator, and the working substance compressed isothermally (curve DA), until the point A is reached, the heat Q_2 being rejected, and the working substance returning to its initial state. The cycle is completed.

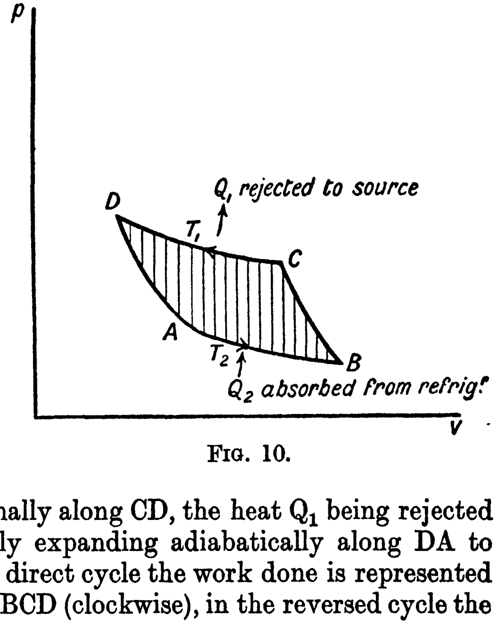

FIG. 10.

Since all the operations are conducted reversibly, it follows from § 24 that the cycle may be conducted in the reversed sense, beginning at A (Fig. 10), expanding along AB, with absorption of heat Q_2 from the refrigerator, compressing adiabatically along BC till the temperature rises to T_1, compressing isothermally along CD, the heat Q_1 being rejected to the source, and finally expanding adiabatically along DA to the initial state. In the direct cycle the work done is represented by the area of the loop ABCD (clockwise), in the reversed cycle the work *spent* is represented by the same area (counterclockwise, see § 13).

26. The Second Law of Thermodynamics.—*It is impossible to construct a machine which shall work in cycles and produce no effects other than the abstraction of heat from a reservoir and the raising of a weight.*

Let us now apply the two laws of thermodynamics to Carnot's cycle.

1. The cyclic process is *isenergic*, $\Delta U = 0$, $\therefore Q_1 - Q_2 = A$. (*First Law.*)

2. In the application of the *Second Law* we establish two propositions:

(*a*) *Of all possible heat engines working with fixed temperatures of source and refrigerator none can be more efficient than a reversible Carnot's engine.*

The *efficiency* of a heat engine is measured by the fraction of the quantity of heat absorbed from the source which is converted into work: $N = A/Q_1$.

$$\text{In a } \textit{cycle} \quad A = Q_1 - Q_2, \therefore N = (Q_1 - Q_2)/Q_1 \quad . \quad . \quad . \quad (43)$$

Let $[\alpha]$ and $[\beta]$ be two engines with same source and refrigerator. $[\alpha]$ is a reversible Carnot's engine, $[\beta]$ any other engine. If possible let $[\beta]$ be more efficient than $[\alpha]$.

Let each engine be arranged to absorb the same heat Q_1 per cycle. Let $[\beta]$ work $[\alpha]$ backwards. This is possible since $[\alpha]$ is a reversible engine. In a complete cycle the compound engine performs the following operations:

$[\beta]$	$[\alpha]$
takes heat Q_1 from the source.	returns heat Q_1 to the source.
does work A'.	absorbs work A.
rejects heat Q_2' to the refrigerator.	takes up heat Q_2 from refrigerator.

The efficiency of $[\beta]$ is $N_\beta = A'/Q_1$, that of $[\alpha]$ $N_\alpha = A/Q_1$, where $N_\beta > N_\alpha$ by hypothesis. Thus $A' > A$. But $A' + Q_2' = A + Q_2 = Q_1$ by the first law, hence $Q_2' < Q_2$.

Thus, the compound engine does work $A' - A$ and absorbs heat $Q_2 - Q_2'$ from the refrigerator. This result is not in contradiction to the first law, but contradicts the second, hence $N_\alpha \leqq N_\beta$.

(*b*) *All reversible engines working in cycles with the same temperatures of source and refrigerator are equally efficient.*

Let $[\beta]$ now be a *reversible* engine. We have shown that $[\beta]$ cannot be more efficient than $[\alpha]$. But the functions of the engines may now be interchanged, $\therefore$ $[\alpha]$ cannot be more efficient than $[\beta]$ $\therefore$ $[\alpha]$ and $[\beta]$ are equally efficient.

27. **Moutier's Theorem.**—*The work done in any isothermal reversible cycle is zero:*

$$(A)_T = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44)$$

For if $(A)_T > 0$, the result is incompatible with the Second Law of Thermodynamics. If $(A)_T < 0$, the result is possible if the cycle is irreversible, since we can always waste work by friction. But if the cycle is *reversible*, we can carry it out in the opposite sense, and then $(A)_T > 0$, which is impossible. Hence $(A)_T = 0$ in an isothermal reversible cycle.

Since the process is a cycle, $A = Q_1 - Q_2$, hence the [illegible] sum of the quantities of heat absorbed or emitted during an isothermal cyclic process is zero :

$$(Q)_T = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (44a)$$

which is a second form of Moutier's theorem.[1]

28. **Absolute Temperature.**—Carnot's investigation shows that *the efficiency of a perfectly reversible engine depends only on the temperatures of its source and refrigerator.* We can therefore *define* these temperatures, in terms of a reversible engine, in such a way that they are absolute, and independent of any particular thermometric substance (Hg, air, H_2, etc.). We have some choice of definition, but it is desirable to make the result fit in as nearly as possible with existing scales. The best of these is that of the gas thermometer. Now :

$N = (Q_1 - Q_2)/Q_1 = 1 - Q_2/Q_1$, a function of T_1 and T_2 only (Carnot), $\therefore Q_1/Q_2 = F(T_1, T_2)$.

The simplest choice of $F(T_1, T_2)$ which is compatible with the gas scale is :

$$Q_1/Q_2 = T_1/T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

This equation fixes *the ratio of the two temperatures.* Then :

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

Similarly, $(Q_2 - Q_3)/Q_2 = (T_2 - T_3)/T_2$ and so on. Divide the first equation by the second : $(Q_1 - Q_2)/(Q_2 - Q_3) = (T_1 - T_2)/(T_2 - T_3)$. Let $Q_1 - Q_2 = Q_2 - Q_3$, then $T_1 - T_2 = T_2 - T_3$. We can easily see that this *definition of equal intervals of temperature* is equivalent to the following: The *differences* between the temperatures of a succession of heat reservoirs are equal when equal amounts of work are done by each of a series of reversible engines working between them and arranged so that the $(n + 1)$th engine receives the heat rejected by the nth one.

The *zero of absolute temperature* (" absolute zero ") is also fixed by the definition. Put $T_2 = 0$ in (46), then $(Q_1 - Q_2)/Q_1 = 1$, $\therefore Q_2 = 0$. The temperature of the refrigerator is zero when *all* the heat absorbed from the source is converted into work. T is essentially positive. It is only when a reservoir at the absolute zero is available that the *whole* of a given quantity of heat can be converted into work.

The *size of the degree* is obviously perfectly arbitrary. If T_1' is the temperature of water boiling under 1 atm. pressure, and T_2' is the temperature of melting ice at the same pressure, we shall put $T_1' - T_2' = 100$, so that the degree shall be the *Centigrade degree.* To make the scale correspond with the gas scale we shall see (§ 35) that we must put $T_2' = 273°$ (or 273·09° exactly, § 51).

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[1] J. Moutier, *Bulletin de la Société philomathique*, August 11th, 1875.

Equation (46) [1] may be regarded as *the fundamental quantitative expression of the Second Law of Thermodynamics.*

The formula may be applied in considering the efficiency of a *refrigerator, i.e.*, a mechanism which is used to abstract heat from a body (*e.g.*, water, in its conversion into ice) and to give up this heat to a warmer body. This is usually effected by making use of the latent heat of evaporation of liquefied ammonia or carbon dioxide, the gas being then reliquefied by compression and the heat evolved communicated to cooling water. The *efficiency* of a refrigerator is measured by the ratio *heat extracted from cold body/work expended* $= Q_2/A = Q_2/(Q_1 - Q_2) = T_2/(T_1 - T_2)$ for reversible working. This fraction is greater the smaller the value of $T_1 - T_2$, so that it is more economical to cool the whole mass through a small drop in temperature than to cool a portion to a lower temperature and then mix this very cold part with the rest. If $T_1 - T_2$ is very small, Q_2 is much larger than A. Work may be obtained by means of a cold body, such as an iceberg, available as a cold reservoir. Conversely, to cool a body below the temperature of its surroundings requires the expenditure of work, and if this is produced by a heat engine, of fuel.[2]

29. Clapeyron's Equation.—Let heat δQ be absorbed by unit mass of a fluid which is undergoing a reversible change of state. We have then: $\delta Q = c_v dT + l_v dv$. Suppose T is constant, whilst p varies according to the characteristic equation, then $\delta Q_T = l_v \delta v$, where l_v is the *latent heat of expansion.*

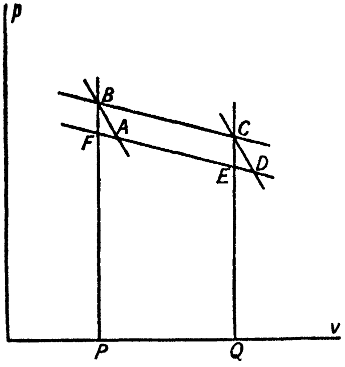

FIG. 11.

Suppose unit mass of fluid taken round a small reversible Carnot's cycle ABCD, between the temperatures T and $(T - \delta T)$. If the changes are small, ABCD (Fig. 11) may be regarded as a parallelogram (*i.e.*, we neglect quantities of the *third* order in comparison with those of the *second*). $\delta v = PQ =$ the small increase in volume, and $\delta Q = l_v dv$ the small amount of heat absorbed at the absolute temperature T.

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[1] On the thermodynamic definition of temperature, cf. Bryan, "Thermodynamics," pp. 45 ff.

[2] Lucke, "Engineering Thermodynamics," p. 1142; Inchley, "Theory of Heat Engines," Ch. VII.; *F. S.*, 1922, **18**, 139 ff.

The *work done* in the cycle is (δA) = area ABCD = area FBCE = FB . PQ.

But FB = increase of pressure per δT rise in temperature at constant volume $= (\partial p/\partial T)_v \,.\, \delta T$, and $PQ = \delta v$

$$\therefore \qquad (\delta A) = \left(\frac{\partial p}{\partial T}\right)_v \delta T \delta v = \left(\frac{\partial p}{\partial T}\right)_v \delta T \frac{\delta Q}{l_v}.$$

But $$(\delta A) = \delta Q \frac{\delta T}{T}, \text{ by the Second Law,}$$

$$\therefore \qquad l_v = T\left(\frac{\partial p}{\partial T}\right)_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

This important equation[1] is a quantitative expression of the Second Law which applies to a large number of experimental cases.

30. Difference of Specific Heats of a Fluid.—From (20) and (47):

$$c_p - c_v = T(\partial v/\partial T)_p(\partial p/\partial T)_v \quad . \quad . \quad (48)$$

$$= -T(\partial v/\partial T)_p{}^2/(\partial v/\partial p)_T \quad . \quad (49)$$

$$= -T(\partial v/\partial T)_p{}^2\,(\partial p/\partial v)_T \quad . \quad (50)$$

from (29), giving the difference of specific heats at constant pressure and at constant volume in terms of the coefficients of expansion and of compressibility (or elasticity).[2]

Now, the coefficient of cubical expansion

$$= (\partial v/\partial T)_p/v_0 = a$$

and the coefficient of isothermal compressibility

$$= -(\partial v/\partial p)_T/v_0 = \eta_T$$

$$\therefore \qquad c_p - c_v = T\alpha^2 v_0/\eta_T = T\alpha^2/\eta_T\,\rho \quad . \quad . \quad (50a)$$

where ρ = density.

In the case of mercury at 0°:

$c_p = 0{\cdot}0333$ gm. cal.; $T = 273$; $v_0 = 1/13{\cdot}595$; $a = 1{\cdot}812 \times 10^{-4}$;
$\eta = 3{\cdot}9 \times 10^{-6}$ c.c. per atm. $= 3{\cdot}9 \times 10^{-6}/1013225$ c.c. per dyne per cm².

$$\therefore \ (c_p - c_v) = \frac{273 \times 1013225 \times (1{\cdot}812 \times 10^{-4})^2}{3{\cdot}9 \times 10^{-6} \times 13{\cdot}595 \times 4{\cdot}184 \times 10^7} \text{ cals.}$$

$$= 0{\cdot}0041 \text{ gm. cal.}$$

$$\therefore \ c_v = 0{\cdot}0333 - 0{\cdot}0041 = 0{\cdot}0292 \text{ cal.}$$

$$\therefore \ c_p/c_v = 1{\cdot}14.$$

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[1] B. P. E. Clapeyron, *Journ. de l'Ecole polytechnique*, Paris, 1834, **14**, 173; transl. in Taylor's "Scientific Memoirs," vol. 3.

[2] Cf. Kleiber, *A. P.*, 1915, **46**, 1054; Tyrer, *C. S.*, 1913, **103**, 1675; 1914, **105**, 2534; *Z. p. C.*, 1914, **87**, 169.

31. Effect of Pressure on Specific Heat.—From (16) and (19) $du = c_v dT + (l_v - p)\,dv$, a perfect differential. Thence (§ 12):

$$(\partial c_v/\partial v)_T = \partial(l_v - p)_v/\partial T$$

$\therefore$ from (47) $$(\boldsymbol{\partial c_v/\partial v})_T = T(\boldsymbol{\partial^2 p/\partial T^2})_v \quad . \; . \; . \quad \textbf{(51)}$$

Again:

$du = \delta Q - \delta A = (c_p dT + l_p dp) - pdv \quad \therefore$ from (II. *b*) § 18:

$du = [c_p - p \,.\, (\partial v/dT)_p]\,dT + [l_p - p \,.\, (\partial v/\partial p)_T]\,dp$

a perfect differential. Thence (§ 12):

$$\frac{\partial}{\partial p}[c_p - p \,.\, (\partial v/\partial T)_p]_T = \frac{\partial}{\partial T}[l_p - p(\partial v/\partial p)_T]_p.$$

Differentiate, and substitute from (47), (29), and (32):

$$l_p = l_v/(\partial p/\partial v)_T = T(\partial p/\partial T)_v/(\partial p/\partial v)_T = -T(\partial v/\partial T)_p$$

$$\therefore \quad \partial l_p/\partial T = -(\partial v/\partial T)_p - T(\partial^2 v/\partial T^2)_p$$

$$\therefore \quad (\boldsymbol{\partial c_p/\partial p})_T = -T(\boldsymbol{\partial^2 v/\partial T^2})_p \quad . \; . \; . \quad \textbf{(52)}$$

Equations (51) and (52) give the effects of changes of volume and pressure on the specific heats. The effect of temperature, *i.e.*, $(\partial c_v/\partial T)_v$ and $(\partial c_p/\partial T)_p$ cannot be calculated by thermodynamics.

Experimental results in this field are very scanty. The earlier results[1] are somewhat contradictory: the general conclusion is that c_p increases with pressure up to a maximum peculiar to each gas and then decreases. At reduced pressures[2] the ratio c_p/c_v decreases with reduction of pressure. The effect of pressure on c_v has been investigated by Joly.[3] His results are:

Air . . . . . $c_v = \cdot 17151 + \cdot 02788\rho$ (ρ = density).
CO_2 . . . . . $c_v = \cdot 16577 + \cdot 2064\rho$.
H_2 . . . . . c_v decreases with increasing density.

The best results yet obtained are probably those of Holborn and Jacob.[4] For air, at 59° C. and a range of pressures from 0—200 kg./cm²., their results are expressed by:

$$c_p \times 10^4 = 2413 + 2{\cdot}86p + \cdot 0005p^2 - \cdot 00001p^3,$$

where p is in kg./cm². Thus c_p increases from $(0{\cdot}2416)_{p\,=\,1}$ to $(0{\cdot}2925)_{p\,=\,200}$. The empirical equations of Vogel[5] and Noell[6] also agree quite well with Holborn and Jacob's results. For nitrogen at a temperature of 81° K. Valentiner[7] finds:

$$c_p = \cdot 2476 + \cdot 000451p - \cdot 0346\,p/s$$

where p/s = actual pressure/saturation pressure.

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[1] Regnault, *Mém. de l'Acad.*, 1862, **26**, 1; Lussana, *Fortschritte der Phys.*, 1896, **1**, 345; 1897, **1**, 331; *N. C.*, 1905, **10**, 192; Witkowski, *P. M.*, 1896, **41**, 288; Koch, *A. P.*, 1908, **26**, 551; *ibid.*, **27**, 311.

[2] Keutel, *Diss.*, Berlin, 1910; Thibaut, *A. P.*, 1911, **35**, 347; Schöler, *A. P.*, 1914, **45**, 913.

[3] *P. R. S.*, 1890, **48**, 440; 1888, **45**, 33; 1894, **55**, 390; *P. T.*, 1891, **182**, 73.

[4] *B. B.*, 1914, **1**, 213.

[5] *Mitt. Forsch. deut. Ing.*, 1911, 108 and 109.

[6] *Sitz. Kgl. Bayer. Akad.*, 1913, 213.

[7] *A. P.*, 1904, **15**, 74.

EXAMPLES V.

1. Show that:

$$c_p = p(\partial v/\partial T)_p + (\partial u/\partial T)_p\,; \quad l_p = p(\partial v/\partial p)_T + (\partial u/\partial p)_T$$

and interpret the meaning in words.

2. Show that $(\partial c_v/\partial v) = \partial^2 u/(\partial u \partial T)$ for a fluid.

3. Show that $\gamma_v = p + (\partial u/\partial v)_p$ and interpret in words.

4. Show that $(\partial u/\partial v)_T = T^2 \dfrac{\partial}{\partial T}\left(\dfrac{p}{T}\right)_v$. The second law is required.

5. Show that if $p/T = f(v)$ is the characteristic equation of a fluid the intrinsic energy will be independent of the volume.

6. An ideal air engine works on the following cycle: air is taken into the cylinder at 1 atm. pressure and 12·8° C., and is compressed adiabatically according to the equation $pv^{c_p/c_v} = \text{const.}$ until the pressure rises to 37·4 atm. Heat is then taken in at constant pressure and then the air expands adiabatically to 5 times its volume. The air is then exhausted at the end of the expansion stroke, the heat being rejected at constant volume. Find the percentage of heat converted into work, assuming $c_p = 0{\cdot}2375$ and $c_v = 0{\cdot}1691$.

7. The coefficient of expansion of pentane is $15{\cdot}9 \times 10^{-4}$; its compressibility is 314×10^{-6} megabar^{-1} at 20°. Find the latent heat of expansion.

8. A reversible engine works between the temperatures 200° and 20°. Find the thermodynamic efficiency.

9. Show that if η_θ and η_Q are the isothermal and adiabatic compressibilities of any substance:

$$\eta_\theta = \eta_Q + T\,(\partial v/\partial T)_p{}^2/c_p v.$$

The adiabatic compressibility of ether at 0° C. is $114{\cdot}45 \times 10^{-6}$ atm.$^{-1}$, the density is 0·7362, the specific heat 0·5290, and $(\partial v/\partial T) = 0{\cdot}0_2 203$. Find η_θ.

10. Find the ratio c_p/c_v for CS_2 given the following data: coefficient of cubical expansion $= 0{\cdot}00114$; compressibility $= 78 \times 10^{-6}$ atm.$^{-1}$; density $= 1{\cdot}292$ (Thorpe), all figures referring to a temperature of 0° C. The value of c_p is related to the temperature t° C. by the equation (Regnault) $c_p = 0{\cdot}2352 + 0{\cdot}000162t$.

11. The following values apply to bromine:

$c_p = 0{\cdot}1071$; density $3{\cdot}102/25°$; coefficient of expansion $0{\cdot}0_2 104$; compressibility $52{\cdot}6 \times 10^{-6}$ atm.$^{-1}$. Find c_v in cal.

12. The specific heat of copper at constant pressure is (50°) 0·0936; the density is 8·93, the coefficient of cubical expansion $0{\cdot}0_4 5142$, the compressibility $0{\cdot}54 \times 10^{-6}$ megabar^{-1}. Find c_v and the ratio c_p/c_v.

13. Integration of equation (52) gives $c_p - c_1 = -T\displaystyle\int_1^p \left(\frac{\partial^2 v}{\partial T^2}\right) dp$, c_p being the specific heat of a gas under a constant pressure p and c_1 the specific heat under a pressure of 1 atmosphere. The value of $(d^2v/dT^2)_p$ may be calculated from any equation of state. Using van der Waals' equation, calculate the value of c_p when p = 50, 100, and 200 atm., for a mixture of $N_2 + 3H_2$, given that $c_1 = 0{\cdot}80$ and that the constant *a* in van der Waals' equation = 0·6 (vol measured in litres at 27° C.).

14. The specific volume of mercury is given by

$$v_\theta = v_0[1 + 0{\cdot}0181618/100 + 0{\cdot}0_4 78(\theta/100)^2.]$$

The specific heat at 1 atm. is given by $0{\cdot}033458 - 0{\cdot}0_4 1074\theta + 0{\cdot}0_7 385\theta^2$, and the density at 0° is 13·5955. Find the specific heat at 25° C. under 100 atm. pressure.

15. The coefficient of pressure β, where $p_\theta = p_0(1 + \beta\theta)$, for carbon dioxide is $0{\cdot}0_2 373$. Find the latent heat of expansion at 0° C. and 1 atm. pressure.

16. The coefficients of expansion α, densities ρ, and compressibilities η of the following elements are given. Calculate $c_p - c_v$ (compressibilities per megabar = 10^6 dynes/cm.^{2}):

	Al	Cu	Hg
$\eta \times 10^6$ . . .	1·3	0·54	3·71
$\alpha \times 10^6$ . . .	76·5	50·1	181·7
ρ (15° C.) . . .	2·65	8·93	13·584

CHAPTER VI

The Ideal Gas

32. Thermodynamics of Gases.—In the development of thermodynamics a prominent part has been played by *gases*, which exhibit a simpler behaviour than liquids or solids. Many of the properties of *dilute solutions* will later be shown to follow equations very similar to those which hold for gases. In the present chapter the properties of gases will be considered in detail, and for simplicity an *ideal gas*, to which all actual gases may be supposed to approach in the limiting case of low pressures, will first be studied. The consideration of the deviations of actual gases from the ideal state will be taken up in Chapter VIII.

33. The Ideal Gas.—The definition of an ideal gas may be framed in more than one way; we shall define it as *a gas which obeys Boyle's law and Joule's law.*

Boyle's Law.—By experiments with the well-known U-tube containing air confined by mercury, Robert Boyle,[1] in 1662, showed that for pressures varying from 30 inches of mercury to $117\frac{9}{16}$ inches (1 atm. = 30 in.) the pressure of a given quantity of gas varies inversely as the volume when the temperature is constant. By making use of a straight tube, containing air, which could be raised from a trough of mercury, Boyle showed that the same law held down to pressures of $1\frac{1}{4}$ in. of mercury. The results may be summarised in the equation (Boyle's Law):

$$pv = const. = k_1 \quad (\mathrm{T\ constant}) \quad . \quad . \quad . \quad . \quad [53]$$

Later experimenters found deviations from Boyle's Law. The following table shows the relative volume which the particular gas will occupy when the pressure is reduced from the given value to atmospheric, the temperature being 16° C.[2]

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[1] "New Experiments Physico-Mechanical touching the Spring and Weight of the Air," second ed., Oxford, 1662. The experiments are contained in an appendix: "A defence of the doctrine . . . against the objections of Franciscus Linus," which is not contained in the first edition (1660). "Works," ed. Birch, fol., 1744, i., 100 ff. The same law, with the same experiments and analogies as those given by Boyle, was put forward, without any claim to novelty, by Mariotte in 1676 ("Oeuvres de Mariotte," Leyden, 1717, *t.* I., 149 ff.).

[2] Cochrane, in "Physical and Chemical Data of Nitrogen Fixation," H.M. Stationery Office, 1918; cf. Amagat, *A. C. P.*, 1893, **29**, 68, 505; Kamerlingh Onnes, etc., references in Jellinek, "Phys. Chem.," I., 334 ff.; Preston, "Theory of Heat."

Gas.	1 atm.	50 atm.	100 atm.	150 atm.	200 atm.
Ideal	1	50	100	150	200
H_2	1	48·5	93·6	136·3	176·4
N_2	1	50·5	100·6	147·6	190·8
Air	1	50·9	101·8	150·3	194·8
O_2	1	—	105·2	—	212·6
O_2 (0° C.)	1	52·3	107·9	161·9	218·8
CO_2	1	69·0	477[1]	498[1]	515[1]

The results show that, with the exception of hydrogen, all the gases named are at first more compressible than an ideal gas, but at high pressures all gases are less compressible than an ideal gas. Helium at moderate pressures shows almost exact agreement with Boyle's Law ; neon is less compressible and behaves like hydrogen, which Regnault called a " gaz plus que parfait."

Joule's Law.—In 1845 Joule carried out experiments to test the validity of Mayer's (implicit) assumption (§ 19) that the energy of a gas is independent of the volume.[2]

If a volume of gas is allowed to expand without doing external work, $\Sigma A = 0$. If the energy of the gas is independent of the volume, $\Delta U = 0$

$\therefore \quad \Sigma Q = \Delta U - \Sigma A = 0$, *i.e.*, no heat should be absorbed or emitted.

Two copper vessels, A and B (Fig. 12), the first containing air at 22 atm. pressure, and the second vacuous, were immersed in a can of water. On opening the taps in C connecting them, expansion occurred, but after stirring the water its temperature was unchanged : " no change of temperature occurs when air is allowed to expand without developing mechanical power " [*i.e.*, doing external work]. The globes and the taps were then placed

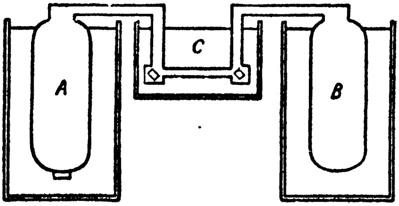

FIG. 12.

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[1] Liquid at pressures greater than 90 atm.

[2] *P. M.*, 1845, **26**, 369. The experiments were finished before Mayer's first reference to Gay Lussac's earlier work was made. Cf. notes to §§ 6, 19. Leslie (" Experimental Enquiry into the Nature and Propagation of Heat," 1804, p. 533) found that the change in temperature produced when hydrogen rushes into a receiver exhausted to 0·1 atm. is the same as that produced by air. Gay Lussac (*Mémoires d'Arceuil*, i., 1807), allowed air, carbon dioxide, and oxygen to rush from one globe into a vacuous globe, and observed the changes on two thermometers at the centres of the globes. The cooling in the first globe was very nearly equal to the heating in the second globe, the maximum change of temperature being in all cases less than 1° C. The results depended on the positions of the thermometers, and the conclusions drawn were erroneous. The correct explanation was first given by Joule.

in three separate cans of water, as shown, and the experiment repeated. A fall of 0·595° C. per kgm. of water occurred in A, a rise of 0·606° C. in B, and a rise of 0·078° C. in C. Within the limits of error the same amount of heat is absorbed by the air expanding from A and doing work as is evolved by the compression of the gas in B. Thus $\Sigma Q = 0$.

Since Joule's thermometer would not record changes less than 1·88° C. *in the air*,[1] Lord Kelvin, in 1851, suggested modifications of the method, and in 1852–1862 he and Joule carried out, in Joule's brewery, at Salford, the "porous-plug" experiments described in § 43. These showed a slight cooling with air and CO_2 and a slight heating with H_2. For permanent gases the result of Joule's first experiment may be taken as very nearly correct: *the intrinsic energy of a gas is independent of the volume* (temperature constant):

$$(\partial u/\partial v)_T = 0 \quad \text{(Joule's Law)} \quad . \quad . \quad . \quad . \quad . \quad [54]$$

An *ideal gas* is one which obeys equations [53] and [54].

We may now apply the two Laws of Thermodynamics.

First Law.—Equation (19) gives:

$$(\partial Q/\partial v)_T \equiv l_v = (\partial u/\partial v)_T + p = p \quad . \quad . \quad . \quad [55]$$

Second Law.—Clapeyron's equation (47), and [55] give:

$$l_v = T(\partial p/\partial T)_v = p \quad \therefore \quad (\partial p/\partial T)_v = p/T \quad . \quad . \quad [55a]$$

$$\therefore \qquad \ln p = \ln T + f(v)$$

$$\text{or} \qquad p = k_2 T \quad (v \text{ constant}) \quad . \quad . \quad . \quad . \quad . \quad . \quad [56]$$

where k_2 is a constant.[2]

A combination of [53] and [56], representing the state of a given mass of gas at any pressure, volume, and temperature, is known as the *general gas law*.

Let the initial volume, pressure, and absolute temperature be p_1, v_1, T_1, and let the state be changed to p_2, v_2, T_2, in two steps:

(i.) Keeping $v = v_1$ change T_1 to T_2 and let p_1 have changed to p. Then by [56]:

$$p = k_2 T_2 = p_1 T_2/T_1$$

---

[1] In Gay Lussac's, and in Leslie's experiments, the temperatures were measured in the gases (air, H_2, CO_2) and were constant to about 0·1° C.

[2] This result is equivalent to the law known as Charles's or Gay Lussac's, that the coefficient of expansion is the same for all gases (see § 33). In 1801 Dalton found the same value for the coefficient of expansion of air as Gay Lussac, whose experiments were published a year later. The results obtained by Charles were never published but communicated verbally to Gay Lussac; he found by means of rather crude experiments that carbon dioxide and air expand equally for equal elevations of temperature (Dixon, *M. M.*, 1891, **4**, 36).

(ii.) Keeping $T = T_2$, change v_1 to v_2. Then p changes to p_2, and from [53]:

$$pv_1 = p_2v_2 = k_1 \quad \therefore \; p_1v_1T_2/T_1 = p_2v_2$$
$$\therefore \; p_1v_1/T_1 = p_2v_2/T_2.$$

Thus, generally, $pv/T = const.$

The value of the constant depends on the quantity of gas, but since a mol of *any* gas exerts the same pressure at the same temperature when confined in the same volume (Avogadro's law) [1] we may conveniently define the constant for 1 mol; it then has the same value for all gases (assumed ideal); and is known as the *gas constant*, R. Thus:

$$pV = RT \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad [57]$$

If p and T are constant, the volume is proportional to the quantity of gas, hence for n mols:

$$pV = nRT \quad . \; . \; . \; . \; . \; . \; . \; . \quad [57a]$$

If m is the mass of gas, M the molecular weight, $n = m/M$, hence

$$pV = RT(m/M) \quad . \; . \; . \; . \; . \; . \quad [57b]$$

or, for unit mass:

$$pv = RT/M \quad . \; . \; . \; . \; . \; . \; . \quad [57c]$$

where v is the *specific volume*; V in [57] is the *molecular volume.*

34. The Gas Constant, R.

The numerical value [2] of R depends on the standard adopted for atomic weight. If oxygen = 16·000, then M is 32. At 1 standard atmosphere pressure and at the temperature of melting ice, 32 grams of oxygen occupy a volume of 22,412 c.c. (corrected for a slight deviation from the ideal state, see § 51):

$\therefore p = 1$, $T = 273{\cdot}09$, $V = 22{\cdot}412$ litres.
$\therefore R = 1 \times 22{\cdot}412/273{\cdot}09 = 0{\cdot}08207$ lit. atm./degree C.
$= 0{\cdot}08207 \times 1013{\cdot}25 \times 10^6 = 8{\cdot}3156 \times 10^7$ erg/1° C.
$= 0{\cdot}08207 \times 1033280 = 84801$ gm. cm./1° C.
$= (8{\cdot}3156 \times 10^7)/(4{\cdot}184 \times 10^7) = 1{\cdot}9875$ gm. cal./1° C.
$= 8{\cdot}3156$ joules/1° C.

35. The Gas Scale of Temperature.—If a is the coefficient of expansion of an ideal gas (§ 30) then we define the *gas temperature* as:

$$(T) = \theta° \text{ C.} + 1/a \quad . \; . \; . \; . \; . \; . \; . \quad [58]$$

From (29), putting $\theta = T$, and $(\partial v/\partial p)_T = -\, v/p$, from Boyle's law, we find:

$$(\partial v/\partial T)_p = v(\partial p/\partial T)_v/p = v/T \text{ from [55a], or } (\partial v/\partial T)_p/v = 1/T.$$

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[1] See the author's "Textbook of Inorganic Chemistry," Macmillan & Co., Chapter IX.

[2] Cf. Henning, *Z. P.*, 1921, **6**, 69.

Let $T = T_0$, the temperature of melting ice, and let v then be v_0, then:

$$(\partial v/\partial T)_p/v_0 \equiv a = 1/T_0 \quad . \quad . \quad . \quad . \quad . \quad [58a]$$

But $$T = \theta + T_0 \text{ and } (T) = \theta + 1/a$$

$$\therefore \quad T = (T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [58b]$$

i.e., the gas temperature, measured on an ideal gas thermometer, is the same as the absolute temperature.

Special experiments (§ 51) give $1/a = 273{\cdot}09 = T_0$.

The coefficient of expansion of an ideal gas has the value $1/273{\cdot}09 = 0{\cdot}003662$.

The following table shows how far the measured values for actual gases deviate from the ideal value:

Gas (at 0°—100°)	a (at 1 atm.).	β.
Ideal gas . . .	0·003662 ...	0·003662
Hydrogen . . .	0·003661 ...	0·003663
Nitrogen	0·003677 ...	0·003675
Carbon dioxide . .	0·00372 ...	0·00373
Sulphur dioxide . .	0·00390 ...	0·00385

The figures under β are the values of the pressure coefficient:

$$\beta = (\partial p/\partial T)_v/p_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (59)$$

For the ideal gas $$p = RT/vM$$

$$\therefore \quad (\partial p/\partial T)_v = R/Mv \qquad \therefore \quad \beta = R/p_0Mv$$

$$\therefore \quad \beta = 1/T_0 = a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [60]$$

The actual values of a and β differ slightly from one another and from the value for the ideal gas.[1]

36. **Ratio of Specific Heats of Ideal Gas.**—Equation [54] shows that the specific heat at constant volume, $c_v = (\partial u/\partial T)_v$, in the case of an ideal gas depends only on the temperature, and not on the actual volume (or pressure).

The heat absorbed in the thermal expansion of an ideal gas is:

$$\delta Q = c_v dT + l_v dv = c_v dT + p dv \text{ per gram, from [55],}$$
$$= C_v dT + RT dv/v \text{ per mol.}$$

In *isothermal* expansion from V_1 to $V_2 (dT = 0)$:

$$Q = RT\int_{V_1}^{V_2} \frac{dv}{v} = RT\ln\frac{v_2}{v_1} \quad . \quad . \quad . \quad . \quad . \quad [61]$$

$$= RT\ln(p_1/p_2) \quad . \quad . \quad . \quad [62]$$

[1] Cf. Landolt-Börnstein, "Tabellen"; Jellinek, "Phys. Chem.," I., 354 ff.

In *adiabatic expansion* ($\delta Q = 0$):

$$\therefore \quad 0 = C_v dT + pdV = C_v dT + RT\frac{dv}{v} = C_v dT + (C_p - C_v)\frac{T}{v}dv$$

from [34*a*]. Divide by TC_v: $\therefore \quad \frac{dT}{T} + \left(\frac{C_p}{C_v} - 1\right)\frac{dv}{v} = 0$

or $$\frac{dT}{T} + (\gamma - 1)\frac{dv}{v} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [63]$$

In the integration of [63] we may further assume C_v independent of T (*not* implied in the definition of the ideal gas), $\therefore$ C_p and γ are independent of T

$$\therefore \qquad \int\frac{dT}{T} + (\gamma - 1)\int\frac{dv}{v} = const.$$

or $$\ln T + (\gamma - 1)\ln v = const.$$

or $$Tv^{\gamma - 1} = const. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [64]$$

Thus $$(T_1/T_2) = (v_2/v_1)^{\gamma - 1} = (p_1/p_2)^{(\gamma - 1)/\gamma} \quad . \quad . \quad . \quad [64a]$$

or $$p_2/p_1 = (v_1/v_2)^{\gamma} \text{ or } pv^{\gamma} = const. = k \quad . \quad . \quad . \quad [64b]$$

By means of [64] γ may be found[1] by experiments involving adiabatic expansion.

37. **Experimental Determination of γ by Adiabatic Expansion.**—The first experiments on the determination of γ were made by Clement and Desormes, in 1812, but the results were not published until 1819.[2] A glass globe is fitted with a stopcock and a manometer. The gas is compressed into the globe to a few cm. of mercury above atmospheric pressure. When the temperature has again equalised, the pressure p_1 is read off. The tap is suddenly opened, and the gas allowed to expand adiabatically to atmospheric pressure, P. The tap is at once closed, and the gas allowed to warm up again to the atmospheric temperature. The pressure p_2 is then read off. Now

$$p_1/P = (v_2/v_1)^{\gamma} = (p_1/p_2)^{\gamma}$$

where v_1 and v_2 are specific volumes

$$\therefore \qquad \gamma = \frac{\log p_1 - \log P}{\log p_1 - \log p_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [65]$$

The most accurate experiments made by this method are those of Röntgen (1870–73).[3]

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[1] γ for mixtures, cf. Leduc, *C. R.*, 1915, **160**, 338.

[2] *J. P.*, 1819, **89**, 321; Laplace, "Mécanique Céleste," vol. 5, p. 138.

[3] *A. P.*, 1870, **141**, 552; 1873, **148**, 580.

The method was improved by Lummer and Pringsheim,[1] by Makower,[2] and by the author.[3] A larger globe (60—120 litres) is used, and instead of closing the tap after expansion (which introduces errors) it is left open and the *temperatures* before and after expansion, T_1 and T_2 (absolute) are found by means of a very thin (0·001—0·01 mm. diameter) platinum wire resistance thermometer in the centre of the globe. It is then readily shown from [64a] that:

$$\gamma = \frac{\log p_1 - \log P}{\log (p_1/P) - \log (T_1/T_2)} \quad . \quad . \quad . \quad . \quad [66]$$

A correction must be applied for the radiation to the thermometer from the walls of the globe, amounting to about 0·002 on γ, and since the gases do not obey the laws of ideal gases, a correction is also necessary to reduce the value of γ calculated by [66] to the true value.[4]

This correction is given in § 51. Let γ', corrected for radiation, be the value calculated by [66], and $\gamma = c_p/c_v$ the true value. Then $\gamma = \phi\gamma'$,

where $$\phi = 1 + (\gamma' - 1)\frac{27}{32}\pi\tau^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67)$$

$$\pi = (p_1 + P)/2p_c\,; \; \tau = 2T_c/(T_1 + T_2)$$

p_c and T_c being the critical pressure and the critical temperature (absolute) of the gas.

From the value of γ the separate values of C_p and C_v may be calculated by a modification of [34a], which takes account of the deviations from the ideal state. The correction will be shown (§ 51) to be

$$C_p - C_v = R\left(1 + \frac{27}{16}\pi\tau^3\right) = 1{\cdot}987\left(1 + \frac{27}{16}\pi\tau^3\right) \quad . \quad . \quad (68)$$

where $\pi = p/p_c$; $\tau = T_c/T$.

The value of C_v reduced to the ideal state is:

$$C_v{}^0 = C_v - \frac{27}{32}R\pi\tau^3.$$

The *work done in the adiabatic expansion of an ideal gas* is:

$$A = \int p dv = k\int (dv/v^\gamma) = (p_1v_1 - p_2v_2)/(\gamma - 1)$$
$$= \frac{R}{\gamma - 1}(T_1 - T_2) \text{ per mol} \quad . \quad . \quad . \quad . \quad . \quad [69]$$

38. Velocity of Sound in a Gas.—The velocity of propagation of sound through a fluid is given by the equation[5]:

$$u^2 = -v^2 \,.\, dp/dv = d\rho/dp = \epsilon/\rho \quad . \quad . \quad . \quad (70)$$

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[1] *A. P.*, 1898, **64**, 555.

[2] *P. M.*, 1903, **5**, 226.

[3] *P. Z.*, 1913, **14**, 969; *P. R. S.*, 1921, **100**, 27.

[4] Equation [65] requires no such correction; cf. § 51.

[5] Maxwell, "Theory of Heat," 1897, p. 223 ff.; Rayleigh's "Sound," 1896, II., § 246; Lamb, "Dynamical Theory of Sound," § 59. The formula is a modification by Laplace and Poisson, about or before the year 1807, of the formula, $u = \sqrt{pv}$, due to Newton (*Principia*, II., Prop. 48).

where ϵ = elasticity, and ρ = density = $1/v$, of the fluid at rest.

The *isothermal elasticity* of an ideal gas is found thus :

$$(\partial p/\partial v)_T = -k_1/v^2 \text{ from [53]}$$

$$\therefore \qquad \epsilon_T = k_1/v = p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad [71]$$

The isothermal elasticity of an ideal gas is equal to the pressure.

If we substitute this in (70) we get *Newton's formula* for the velocity of sound :

$$\text{u} = \sqrt{p/\rho} = \sqrt{pv.}$$

This gives for air, at 0° C. :

$p = 76 \times 13{\cdot}59 \times 981 = 1013215$ dynes/cm². approx.

$\rho = 0{\cdot}00129$ gm./cm.³

$\therefore$ u = 280 metres per second.

This value is much too low ; Newton attempted to explain the discrepancy between this and the observed value (i.) by supposing that the sound was propagated with an infinite velocity through the actual solid particles of the air, (ii.) by the effect of vapours floating in the air.

Laplace and Poisson pointed out that the rapid compressions and expansions in the sound wave are *adiabatic* rather than isothermal, so that ϵ_Q must be substituted in [70], not ϵ_T.[1] The *adiabatic elasticity* of an ideal gas is :

$$\epsilon_Q = -v(\partial p/\partial v)_Q$$

$$\text{From [64b]} \qquad (\partial p/\partial v)_Q = -k\gamma/v^{\gamma-1}$$

$$\therefore \qquad \epsilon_Q = \gamma p \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad [72]$$

$$\therefore \qquad \text{u} = \sqrt{\gamma p/\rho} = \sqrt{\gamma pv} = \sqrt{\gamma \text{RT/M}} \quad . \quad . \quad . \qquad [73]$$

$$\text{or} \qquad \gamma = \text{u}^2\text{M/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad [73a]$$

The velocity is independent of p (pv = const.), proportional to $\sqrt{\text{T}}$, and inversely proportional to $\sqrt{\text{M}}$. Taking $\gamma = 1{\cdot}403$, [73] gives for air at 0° C.: u = $280 \times \sqrt{1{\cdot}403} = 331{\cdot}6$ m./sec., in accordance with observed values.

On account of deviations from the gas-laws [73] requires correction. This (§ 51) is given by :

$$\gamma = \frac{\text{u}^2\text{M}}{\text{RT}}\left[1 - \frac{9}{64}\pi\tau(1 - 6\tau^2)\right] \quad . \quad . \quad . \quad . \quad . \qquad (74)$$

where $\pi = p/p_c$; $\tau = \text{T}_c/\text{T}$.

The velocity of sound in free dry air at 0° was found by Hebb[2] to be 31·44 m. per sec., and 331·28 m. per sec. These give, by equation (74), = 1·4039 and 1·4026, respectively, the mean, 1·4033, being almost exactly the value (1·4034) found by the author by the adiabatic method.

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[1] Cf. Amagat, " Notes sur la physique," 1912, p. 3.

[2] *P. R.* 1905, **20**, 89 ; *Trans. Roy. Soc. Canada*, 1919, **13**, iii, 101.

Instead of measuring the velocity in free air, it may be determined in tubes. This method was used by Regnault and others; the most recent determinations are due to Dixon, Campbell and Parker.[1] Corrections for the damping effect of the walls of the tube are then necessary. The result for air at 0° is in good agreement with the above figure; values for this and other gases were found at high temperatures.

Finally, the method of stationary waves may be used. A column of gas in a tube is set in vibration and the positions of the nodal points found, either by the distribution of fine dust in the tube,[2] or by exploring with a hearing tube or by moving a piston along the tube and measuring the positions of maximum and minimum sound. In a method lately used by the author and W. G. Shilling up to 1000° C.[3] the source of sound was a telephone actuated by a valve oscillator which gave a perfectly steady frequency (3000 per sec.). A movable piston and a hearing tube were used.

39. **Limiting Densities.**—Avogadro's law makes the ratio of the weights of equal volumes of two gases, under the same conditions of temperature and pressure, equal to the ratio of the *molecular weights*. In practice it is usual to determine the *normal density*, *i.e.*, the weight in grams of 1 litre of the gas, measured at 0° C. and 1 atm. pressure, the weight being reduced to sea-level and 45° latitude. The ratio of the normal densities of two gases should then be equal to the ratio of the molecular weights, and as 32 is adopted as the molecular weight of oxygen ($O_2 = 32$), the molecular weight of any other gas could be found by a comparison of its normal density with that of oxygen.

In reality, owing to deviations from Boyle's law, resulting in slightly unequal compressibilities, this method will not give exact results, but as the deviations become smaller with diminishing pressure, and, according to experiments of the late Lord Rayleigh,[4] appear to vanish at very small pressures, it may be assumed with some confidence that the ratio of the densities of two gases at very low pressures, *i.e.*, the ratio of the *limiting densities* ($p \longrightarrow 0$), will give the *exact* ratio of the molecular weights (D. Berthelot, 1899).[5]

If a mass W gm. of gas occupies at 0° C. a volume v under a pressure p, the quotient W/pv may be called the *density per unit*

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[1] *P. R. S.*, 1921, **100**, 1.

[2] Kundt, *A. P.*, 1868, **135**, 337, 527; Kundt and Warburg, *ibid.*, 1876, **157**, 353; Wüllner, *ibid.*, 1878, **4**, 321; Strecker (higher temperatures), *ibid.*, 1881, **13**, 20; 1882, **17**, 85; Capstick, *P. R. S.*, 1893, **54**, 101; 1895, **57**, 322; Behn and Geiger, *D. p. G.*, 1907, **9**, 657; Partington, *P. Z.*, 1914, **15**, 601; Partington and Cant, *P. M.*, 1922, **43**, 369; Partington and Shilling, *ibid.*, 1923, **45**, 416.

[3] *F. S.*, 1923, **18**, 386. c_p/c_v for mixtures of gases: Leduc, *C. R.*, 1915, **160**, 338. See "The Specific Heats of Gases," by Partington and W. G. Shilling (Benn Bros., 1924).

[4] *P. T.*, 1901, **196**, 205; 1902, **198**, 417.

[5] *J. P.*, 1899 [iii], **8**, 263; cf. Guye, *J. C. P.*, 1908, **6**, 769; Abegg, "Handbuch der Anorg. Chemie," III, **3**, pp. 22 ff.; Young, "Stoichiometry," 1918, p. 44.

pressure. If the gas obeyed Boyle's law this would be the same at all pressures, since then pv = const. Owing to deviations from Boyle's law, the quotient depends on the pressure. If $p = 1$, we have the normal density; if $p \longrightarrow 0$ the quotient approaches the value for an ideal gas, the *limiting density.* The ratio of the limiting densities of two gases is equal to the ratio of the molecular weights:

$$\mathrm{M}_a : \mathrm{M}_b = W_a/(p_o v_o)_a : W_b/(p_o v_o)_b \quad . \quad . \quad . \quad . \quad (75)$$

where $p_o v_o$ is the limiting value of pv as $p \longrightarrow 0$.

If D is the normal density of a gas, $D = W/p_1 v_1$, where $p_1 v_1$ is the value of pv for $p = 1$

$$\therefore \quad \mathrm{M}_a : \mathrm{M}_b = D_a(p_1 v_1/p_o v_o)_a : D_b(p_1 v_1/p_o v_o)_b \quad . \quad . \quad (76)$$

The ratio $(p_1 v_1/p_o v_o)$ may be determined by two methods[1]:

(i.) For gases deviating only slightly from Boyle's law between zero pressure and 1 atm. (H_2, O_2, N_2, CH_4, CO) the relative deviation from Boyle's law may be assumed to be proportional to the pressure:

$$(p_o v_o - pv)/p_o v_o = Ap \quad . \quad . \quad . \quad . \quad . \quad . \quad (77)$$

where A is a constant for each gas at 0° C., called the *compressibility coefficient.* Its value may be found from two measurements of pv between 1 atm. and zero pressure or may be calculated from the characteristic equation (cf. § 51). Thus, when $p = 1$, $pv = p_1 v_1$,

$$(p_1 v_1/p_o v_o) = 1 - A$$

$$\text{or} \quad \frac{\mathrm{M}_a}{\mathrm{M}_b} = \frac{D_a(1 - A_a)}{D_b(1 - A_b)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (78)$$

	Normal density.		Compressibility coeff.
Hydrogen	0·089873	...	— 0·00054
Oxygen	1·42900	...	+ 0·000964

$$\therefore \frac{\text{lim. dens. H}}{\text{lim. dens. O}} = \frac{\text{mol. wt. } H_2}{\text{mol. wt. } O_2} = \frac{0{\cdot}089873(1 + 0{\cdot}00054)}{1{\cdot}42900(1 - 0{\cdot}000964)} = 1/15{\cdot}876.$$

If $O_2 = 32{\cdot}00$, $H_2 = 32/15{\cdot}876 = 2{\cdot}0156$ $\therefore$ H $= 1{\cdot}0078$, which is in almost exact agreement with the value found by Morley from the synthesis of water.

(ii.) In the case of more compressible gases (CO_2, N_2O, HCl, NH_3) the assumption made in (77) is no longer valid. It is better then to determine $p_o v_o$ by extrapolation of a curve giving pv at various pressures.

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[1] Berthelot, *Trav. et Mém. du Bureau Internat. Poids et Mésures*, 1907, vol. 13; Abegg's "Anorg. Chem.," III, 3, 22 ff.; Gray and Burt, *C. S.*, 1909, 95, 1633; Burt and Edgar, *P. T.*, 1916, 216, 393; Leduc, *A. de P.*, 1918, 9, 5; Guye, *J. C. P.*, 1919, 17, 141.

Normal density of HCl = 1·63915 ; p_1v_1 (for an arbitrary mass of gas) = 54803 ; p_0v_0 (extrapolated) = 55213, hence :

Limiting density of HCl = 1·63915 × (54803/55213) = 1·62698.

Normal density of O_2 = 1·42900, and the following values of p_1v_1, p_0v_0 (extrapolated), and hence the limiting densities of O_2 were found :

p_1v_1.	p_0v_0.	Lim. dens. O_2.
139,628	139,769	1·42756
138,959	139,087	1·42768
56,256	56,311	1·42760
	Mean	1·42762

$$\therefore \text{Mol. wt. of HCl} = 32 \times (1{\cdot}62698/1{\cdot}42762) = 36{\cdot}469,$$

$$\therefore \text{at. wt. of Cl} = 36{\cdot}469 - 1{\cdot}008 = 35{\cdot}461.$$

The value found by the direct synthesis of HCl by Edgar[1] was 35·462, in excellent agreement. The determination of atomic weights by the limiting density method gives results at least as accurate as those found by chemical methods, and in some cases it has disclosed previously unsuspected sources of error in the latter. The atomic weight of silver, which was the real standard in the gravimetric method, formerly taken as 107·94, has been shown to be 107·88, from the values for Cl and N found by the method of limiting densities.

The following table gives the compressibility coefficients of some common gases at 0° C. (Lord Rayleigh) [2] :

Oxygen .	+ 0·00094	Carbon Monoxide	+ 0·00081
Hydrogen	− 0·00053	Carbon Dioxide .	+ 0·00668
Nitrogen .	+ 0·00056	Nitrous Oxide .	+ 0·00747

Burt (1910) gives : Neon, − 0·00105 ; Helium, 0·00000.

Gray and Burt (1910) give : Hydrogen Chloride, + 0·00748.

EXAMPLES VI.

1. Find the values of the gas constant R in the following units : (*a*) 1 cub. ft., 1 lb., 1° F. ; (*b*) 1 cub. ft., 1 oz. ; 1° C.

2. Calculate in calories, joules and gm. cm., the heat absorbed when 50 gm. of oxygen are expanded isothermally at 15° C. from atmospheric pressure to a volume of 100 litres. Find the initial volume and final pressure.

3. Find (1) the work in ergs necessary to compress 60 grams of oxygen isothermally from 20 litres to 1 litre at a temperature of 15° C. and (2) the amount of work done by the gas if allowed to expand again adiabatically to its original volume.

4. Find the work in ergs done under the following conditions : (1) Isothermal expansion of 1 mol of ideal gas from $V_1 = 1$ litre to $V_2 = 10$ litres at 17° C. (2) Adiabatic expansion of 1 mol of oxygen from 1 litre to 10 litres, the initial temperature being 0° C. and the ratio of the specific heats 1·4.

5. Find the value of a litre atmosphere in ergs and in gram centimetres if the density of mercury is 13·596 at 0°.

6. A gas initially at the pressure 800·90 mm. and temperature 19·5° C. is

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[1] *P. T.*, 1908, **209**, 1 ; a continuation of work by Dixon and Edgar, *ibid.*, 1905, **205**, 169.

[2] Cf. Young, "Stoichiometry," London, 1918, p. 45.

allowed to expand adiabatically to pressure 755·6 mm. The temperature immediately after expansion is 14·66°. Assuming ideal gas calculate $\gamma = c_p/c_v$. If the critical pressure and temperature of the gas are 39 atm. and − 140° C., find the corrected value of γ, and calculate C_p, C_v, and $C_v°$.

7. A quantity of argon at 0° C. and 1 atm. is expanded adiabatically to 0·1 atm. Find its final temperature ($\gamma = 1{\cdot}667$).

8. Five litres of a gas at 27° C. are expanded adiabatically to a volume of 6·02 litres at 5° C. Find C_v and C_p (assume ideal).

9. Show that for a gas for which only $pv = \mathrm{RT}$ is assumed :

$$C_p - C_v = \mathrm{R} - \mathrm{p}\left(\frac{\partial C_p}{\partial p}\right)_v + v\ \left(\frac{\partial\ v}{\partial v}\right)_p$$

$$= \mathrm{R} - \mathrm{T}\left(\frac{\partial C_p}{\partial \mathrm{T}}\right)_v + \mathrm{T}\left(\frac{\partial C_v}{\partial \mathrm{T}}\right)_p$$

10. The velocity of sound in O_2 at 0° C. is $3{\cdot}172 \times 10^4$ cm./sec. The density of O_2 at this temperature is 1·42900. What is the ratio of the specific heats of O_2 at this temperature (p = 1 atm.) ?

11. If the velocity of sound in hydrogen is 1286 metres/sec. find C_p/C_v for this gas, if its density is 0·08987 (temp. = 0° C. ; pressure = 1 atm.).

12. The velocity of sound in water at 25° C. is 1457 m./sec. The isothermal compressibility of water is $48{\cdot}9 \times 10^{-6}$ per megabar (10^6 dynes/cm^2.). Find the ratio c_p/c_v for liquid water. The coefficient of expansion is (10°—20° C.) 15×10^{-5} ; confirm the above value for the velocity of sound.

13. The velocity of sound in carbon monoxide at 0° is $3{\cdot}371 \times 10^4$ cm./sec. Find γ on the assumption of ideal gas. The critical pressure and temperature are 35·9 atm. and − 141·1° C. Find a corrected value of γ and calculate C_p and C_v.

14. The half wave-lengths of sound in air and nitrous oxide at 12·25° C. and 1 atm. were found in a particular experiment to be 7·072 cm. and 5·495 cm. Assuming $\gamma' = 1{\cdot}402$ for air, and the critical constants of N_2O as $p_c = 75$ atm., $T_c = 308{\cdot}5°$ K., those of air as $p_c = 39{\cdot}3$ atm. and $T_c = 132{\cdot}6°$ K., find $c_p/_v$, C_v and C_p for the gas.

15. The normal density of N_2O is 1·9777 gm./lit. Find the molecular weight of this gas, given that the normal density of hydrogen is 0·089873. (H = 1.)

CHAPTER VII

Changes of Physical State

40. The Clapeyron-Clausius Equation.—Clapeyron's equation (47) applies to heterogeneous as well as to homogeneous systems. The latent heat of expansion, l_v, is the heat absorbed per unit increase in *volume* of the system, whereas the latent heat of evaporation or fusion, L_e or L_f (§ 5), refers to the change of unit *mass* of one phase into another. Let v_l and v_g be the specific volumes of the liquid and vapour, then, for evaporation :

$$l_v = L_e/(v_g - v_l) \quad \therefore \quad \text{from (47)}$$

$$\mathbf{L_e = T(v_g - v_l)\frac{dp}{dT}} \quad . \quad . \quad . \quad . \quad . \quad \mathbf{(79)}$$

Since $v_g > v_l$, $L_e > 0 \quad \therefore \quad dp/dT > 0$. The *total* differential coefficient dp/dT is used, not $(\partial p/\partial T)_v$, since p depends only on T.

The external work is $p(v_g - v_l)$, hence the increase in intrinsic energy in evaporation is $L_e - p(v_g - v_l) = L_i$, which is called the *internal latent heat.*

Equation (79) was obtained by Clapeyron, W. Thomson, and R. Clausius,[1] and is *exact.*

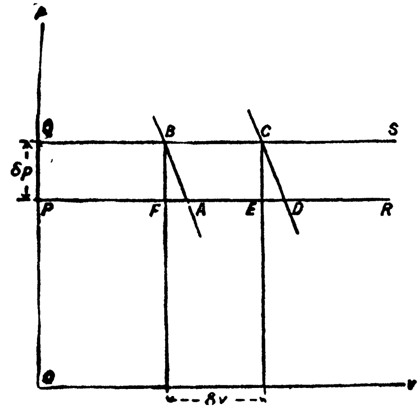

FIG. 13.

Alternative Deduction.—Let a quantity of liquid and vapour be in equilibrium in a cylinder with a piston, under a vapour pressure $p—\delta p$, at a temperature $T—\delta T$.

Let PR, QS (Fig. 13) be the isotherms $T—\delta T$ and T, where P and Q correspond with pressures $(p—\delta p)$ and p. PR and QS are horizontal since, so long as two phases are present, p depends only on T.

Let the system be taken round a reversible Carnot's cycle :

1. Compress adiabatically along AB until the temperature reaches T.

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[1] Clapeyron, *J. de l'Ecole polytechnique*, Paris, 1834, **14**, 173 ; Clausius, *A. P.*, 1850, **81**, 168 ; Thomson, *P. M.*, 1850, **37**, 123.

2. Transfer the cylinder to the hot reservoir and expand isothermally until unit mass of liquid is evaporated; the change in volume is δv = BC, and the heat absorbed is L_e.

3. Transfer to the non-conducting stand and expand adiabatically along CD till the temperature reaches T—δT.

4. Transfer to the cold reservoir and compress isothermally along DA till the initial state is reached.

Since δT is small the segments of the adiabatics AB and DC may be considered straight lines. Draw BF and CE perpendicular to the volume axis.

Work done in cycle = area of parallelogram ABCD
= area of rectangle FBCE = FB × BC.

But FB = increase of pressure at constant volume due to rise of temperature $\delta T = (dp/dT)\delta T$;

and BC = increase of volume due to evaporation of unit mass of liquid = $v_g - v_l$;

∴ work done in cycle $= (dp/dT).\delta T(v_g - v_l) = L_e\delta T/T$ by (46)

$$\therefore\ L_e = T\,(v_g - v_l)\,.\,dp/dT \quad . \; . \; . \; . \; . \quad (79)$$

Example.—Evaporation of water at 100° C. under 1 atm. pressure:

T = boiling point = 273 + 100 = 373;

v_g = sp. vol. of saturated vapour = 1674 c.c. (Watt, in 1763, found 1800 c.c.);

v_l = sp. vol. of liquid = 1 c.c. very nearly;

$\frac{dp}{dT}$ = 27·12 mm. Hg per 1° C. at 100° C.

$= \frac{27{\cdot}12 \times 1{,}013{,}225}{760}$ dyne per cm.^{2} per 1° C.

$\therefore L_e = \frac{373 \times 1673 \times 27{\cdot}12 \times 1{,}013{,}225}{760 \times 4{\cdot}18 \times 10^7}$ gm. cal.

= 539·7 cal. (obsd. 538·7 [1] cal.; Black, in 1764, found experimentally 450; Watt, later, 533 cal.).[2]

Density of Saturated Vapour.—Equation (79) gives an indirect method of finding the *density of saturated vapour*: $\rho = 1/v_g$. A direct method was used by Fairbairn and Tate,[3] and improved by Knoblauch, Linde, and Klebe.[4]

Another method is to make use of the Law of Cailletet and Mathias (§ 47). Young[5] also finds that $\log\,(1/v_g) = A + B \log p$, where p is the vapour pressure, A and B constants for each substance. Or: $d\rho/dp = B\rho/p$. The ratios of the actual densities of vapours to the ideal densities (calculated by the gas laws), have been determined by Young.[6] Numerical data in Winkelmann.[7]

The *latent heat of evaporation per mol* is $\lambda_e = ML_e$, and if $V_l = Mv_l$, $V_g = Mv_g$

$$dp/dT = \lambda_e/T(V_g - V_l) \quad . \; . \; . \; . \; . \quad (80)$$

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[1] Experimental values of L_e: Jellinek, "Phys. Chem.," I., 677.

[2] Cf. Preston's "Heat," 1894, p. 304.

[3] *P. T.*, 1860, **150**, 185; *P. M.*, 1861, **21**, 230.

[4] *Mitteil. Forschungsarbeit. auf d. Gebiet d. Ingenieurwesens*, 1905, **21**, 33.

[5] *Z. p. C.*, 1910, **70**, 620.

[6] *P. M.*, 1892, **33**, 153.

[7] "Physik," III., 962 ff.

V_l may be neglected in comparison with V_g at temperatures not near the critical

$$\therefore\ dp/d\mathrm{T} = \lambda_e/\mathrm{T}V_g \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (81)$$

If the saturated vapour obeys the gas laws (approximately true at *low* temperatures, ∴ low vapour pressures), then $V_g = \mathrm{RT}/p$
$\therefore\ dp/d\mathrm{T} = \lambda_e p/\mathrm{RT}^2$

or
$$\frac{1}{p}\cdot\frac{dp}{d\mathrm{T}} = \frac{d\ln p}{d\mathrm{T}} = \frac{\lambda_e}{\mathrm{RT}^2} \quad . \quad . \quad . \quad . \quad [82]$$

Example.—In the case of water (see above): $\mathrm{R} = 1{\cdot}987$ gm. cal., $p = 760$ mm., $\mathrm{T} = 373$; $dp/d\mathrm{T} = 27{\cdot}12$ mm. per 1°
$\therefore\ \mathrm{L}_e = \lambda_e/\mathrm{M} = (1{\cdot}987 \times 373^2 \times 27{\cdot}12)/(760 \times 18) = 548{\cdot}0$ cal.
This is about 2 per cent. larger than the observed value; under this pressure the vapour is far from ideal.

The following table [1] gives the values of $dp/d\mathrm{T}$ for some common liquids at the boiling point:

Substance.	Boiling Pt. (°K.).	dp/dT mm./1°.	Substance.	Boiling Pt. (°K.).	dp/dT mm./1°.
Chlorine . .	239·4	33·2	Chlorobenzene .	405·0	20·5
Bromine . .	331·75	25·2	Ether . .	307·6	26·9
Mercury . .	629·75	13·4	Acetone . .	330·0	26·4
Ammonia . .	240·1	37·7	Ethyl alcohol .	351·3	30·35
Sulphur . .	717·55	12·2	Ethyl acetate .	350·15	25·1
Sulphur dioxide.	262·9	33·7	Aniline . .	457·4	19·6
Benzene . .	353·2	23·45	Phenol . .	456·0	20·5
Toluene . .	383·7	21·75	Ethyl formate .	327·3	26·6
m-Xylene . .	412·0	21·1	Acetic acid .	391·5	23·9
			Water . .	373	27·12

Integrate [82] on the assumption that λ_e is independent of temperature:

$$\therefore \qquad \ln p = -\lambda_e/\mathrm{RT} + const. \quad . \quad . \quad . \quad . \quad . \quad . \quad [83]$$

or if p_1, p_2 are the pressures at T_1, T_2:

$$\lambda_e = \frac{\mathrm{RT}_1\mathrm{T}_2}{\mathrm{T}_2 - \mathrm{T}_1}\ln\frac{p_2}{p_1} = 4{\cdot}576\,\frac{\mathrm{T}_1\mathrm{T}_2}{\mathrm{T}_2 - \mathrm{T}_1}\log\frac{p_2}{p_1}\ \text{cal.} \quad . \quad [84]$$

The approximation: λ_e *independent of T*, is sufficient only over a very restricted range of temperature (say 10—20°. In the case of water, $\mathrm{L}_e = 538{\cdot}7$ at 100° and decreases by 0·63 cal. per 1° between 90° and 100°). [84] may serve to determine λ_e from the vapour pressures at two temperatures fairly close together, but [83] will not be exact for p except over a restricted range of T. If [83] is put in the form :

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[1] Young, "Distillation Principles and Processes," 1922, p. 14.

$$\log p = A/T + B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [85]$$

the "constant" A really depends on temperature.[1]

A closer approximation is : λ_e *a linear function of T* :

$$\lambda_T = \lambda_0 + aT \ (a \text{ constant}) \quad . \quad . \quad . \quad . \quad . \quad (86)$$

$$\therefore \quad \ln p = \int \frac{\lambda_0 + aT}{RT^2}\, dT = -\lambda_0/RT + (a/R)\ln T + const. \quad [87]$$

$$\therefore \quad \log p = A/T + B \log T + C \quad . \quad . \quad . \quad [87a]$$

where A, B, and C are constants. This equation, due to Kirchhoff,[2] was shown by Juliusburger [3] to apply with a maximum error of 3 per cent. to over 70 substances up to the critical point. It is probably the most useful vapour-pressure equation, and holds also for solutions when the constants are varied with concentration.[4]

Biot's vapour pressure formula (1844) : $\log p = a + b\alpha^{\tau} + c\beta^{\tau}$, where a, b, c, α, β, are constants, and $\tau = \theta°$ C.—*const.*, and Magnus's formula (1844) : $p = ab^{\theta/(\theta + c)}$, where a, b, c are constants, are only of historical interest. Regnault modified Biot's formula to $\ln p = a - b\alpha^{T}$, where α may be taken as 0·9932.

Bertrand's formula (1887)[5] : $p = A[(T - B)/T]^n$, where A, B, and n are constants, gives good results. The value of n may usually be taken as 50.[6] Rankine (1849)[7] used the equation $\log p = \alpha - \beta/T - \gamma/T^2$, where α, β, γ are constants.

Van der Waals' formula (1899)[8] : $\log(p_c/p) = a(T_c/T - 1)$, where p_c, T_c are the critical values and a is 3·0 approximately, although not strictly accurate (cf. § 49), gives useful results.[9] According to Von Jüptner,[10] a is a function of temperature, $a = a_0 - \alpha T/T_c + \beta/(1 - T/T_c)$, α and β being constants. Cederberg [11] puts $a = \alpha\beta^{(T/T_c - \gamma)^2}$, where α, β, γ are constants. Cederberg also uses the formula

$$\log \frac{p}{p_c} = -\frac{\lambda_0}{4{\cdot}57T} + 2{\cdot}5 \ \log T - \frac{\epsilon}{4{\cdot}57} T^{2}$$

where ϵ is a constant.

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[1] Cf. Mortimer, *J. A. C. S.*, 1922, **44**, 1429.

[2] *A. P.*, 1858, **104**, 612.

[3] *A. P.*, 1900, **3**, 618.

[4] Unpublished results of the author and Dr. G. N. White ; *H. M.*, p. 165.

[5] "Thermodynamique," 1887, pp. 157 ff. ; *C. R.*, 1887, **104**, 1568.

[6] A. W. Porter, *P. M.*, 1907, **13**, 724. See also Speranski, *Z. p. C.*, 1913, **85**, 623.

[7] *Edinb. Phil. J.*, 1849, **47**, 28 ; Bose, *P. Z.*, 1907, **8**, 944.

[8] "Kontinuität," 2nd ed., p. 158.

[9] Cf. Porter, *F. S.*, 1922, **18**, 201.

[10] *Z. p. C.*, 1906, **55**, 738 ; 1907, **60**, 101 ; 1908, **63**, 355 ; 1908, **64**, 709 ; 1912, **80**, 299 ; 1913, **85**, 1.

[11] Cf. Nernst, "Grundlagen," p. 125 ; *P. Z.*, 1914, **15**, 697, 824. Another formula has been given by Todd and Owen, *P. M.*, 1919, **38**, 655 ; and a large number are given in Winkelmann's "Physik," vol. 3.

Ramsay and Young's[1] rule is often of value in the interpolation of vapour pressure curves.

Let T_A, T_A' be two absolute temperatures at which the vapour pressures of a substance A have the values p and p';

T_B, T_B' the absolute temperatures at which the vapour pressures of another substance B have the values p and p';

$$\text{then } T_A'/T_B' = T_A/T_B + c\,(T_A' - T_A),$$

where c is a constant, usually very small. In the case of chemically similar substances (C_6H_5Cl and C_6H_5Br; esters) $c = 0$ and $T_A'/T_B' = T_A/T_B$, which gives $(T_A' - T_A)/(T_B' - T_B) = T_A/T_B =$ const., a rule put forward by Dühring (1878). Porter (1907)[2] has shown that Ramsay and Young's rule is true when $f(p) = A - B/T$, where $f(p)$ is any function of pressure which is identical for the substances concerned. This is satisfied by Bertrand's formula (above) when $n = 50$ for all substances. The values of c for different temperatures are not constant for "associated" liquids (water, alcohols, acetic acid).[3]

The value of the constant a in (86) and [87] may be found as follows:

$$\lambda_T = Q = \Delta U + A = \lambda_0 + aT; \quad \text{and } A = RT \text{ (approximately)}$$

$$\therefore \quad \lambda_0 + aT = \Delta U + RT \quad \therefore \quad \Delta U = \lambda_0 + (a - R)T$$

$$\therefore \quad d\Delta U/dT = a - R = C_v\,(\text{vap.}) - c_v\,(\text{liq.}), \text{ from (38a)}$$

$$\therefore \quad a = (C_v + R) - c_v\,(\text{liq.}) = C_p - c_v\,(\text{liq.}) \quad . \quad . \quad . \quad [88]$$

Hence a is equal to the molecular heat of the vapour at constant pressure *minus* the heat capacity of an equal mass of liquid.

41. Heat of Dissociation.—The first application of thermodynamics to chemistry, made by Horstmann in 1869,[4] was to thermal dissociation. In certain systems the pressure, like the vapour pressure of a pure liquid, is a function of temperature only: $p = f(T)$. In such cases all the phases of the system must be of invariable composition, and examples of such types of thermal dissociation are:

(1) NH_4Cl (solid) $\rightleftharpoons NH_3 + HCl$; (2) $CaCO_3 \rightleftharpoons CaO + CO_2$; (3) $CuSO_4, 5H_2O \rightleftharpoons CuSO_4, 3H_2O + 2H_2O$ (vap.).

Such cases as: (4) $N_2O_4 \rightleftharpoons 2NO_2$, are not covered, since the composition, and therefore the pressure, depend on volume as well as temperature (see § 88).

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[1] Ramsay and Young, *P. M.*, 1885, **20**, 515; 1886, **21**, 33, 135; **22**, 32, 37; Herz, *Z. E.*, 1918, **24**, 333; 1919, **25**, 45.

[2] A. W. Porter, *P. M.*, 1907, **13**, 724. See also Speranski, *Z. p. C.*, 1913, **85**, 623.

[3] On vapour-pressure formulæ, cf. Winkelmann, *Physik*, III., **2**, 903–961, Ariès, *C. R.*, 1918, **166**, 447, 553, 668, 802, 935; **167**, 118, 267; Todd and Owen, *P. M.*, 1919, **38**, 655; Meyers, *ibid.*, 1920, **40**, 362; van Liempt, *Z. an. C.*, 1920, **111**, 280; Henglein, *Z. E.*, 1920, **26**, 431; *Z. p. C.*, 1921, **98**, 1; Hofbauer, *Z. p. C.*, 1912, **80**, 117; 1913, **83**, 336.

[4] *B.*, 1869, **2**, 137; *A.*, 1872, **8**, supplt., p. 112; *ibid.*, 1873, **170**, 192; Ostwald's *Klassiker*, No. 137, 1903; Brill, *Z. an. C.*, 1905, **45**, 275; Magnusson, *J. P. C.*, 1907, **11**, 21.

Consider reaction (1). Let V_{NH_4Cl} = molar volume of solid sal ammoniac, V_{HCl} and V_{NH_3} = molar volumes of NH_3 gas and HCl gas. If dissociation is complete, the change of volume per mol dissociated is :

$$\Delta V = V_{HCl} + V_{NH_3} - V_{NH_4Cl} = V_{NH_3} + V_{HCl} = 2RT/p$$

approximately, the volume of the solid being neglected.

The *heat of dissociation* per mol is given by (79) :

$$\lambda_d = T \,.\, \Delta V \,.\, dp/dT = 2RT^2 \,.\, d \ln p/dT$$

If λ_d is constant, $\ln p = -\lambda_d/2RT + \text{const.}$

$$\therefore \qquad \ln \frac{p_2}{p_1} = \frac{\lambda_d}{2R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \; . \; . \; . \; . \; . \quad [89]$$

For n mols of gaseous product (dissociation complete) :

$$\ln \frac{p_2}{p_1} = \frac{\lambda_d}{nR}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \; . \; . \; . \; . \; . \quad [89a]$$

$$\therefore \qquad \log \frac{p_2}{p_1} = \frac{\lambda_d}{4{\cdot}576n}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad . \; . \; . \; . \; . \quad [89b]$$

In case (4) let Q = heat absorbed in the hydration with *liquid* water : $CuSO_4, 3H_2O + 2H_2O(liq.) = CuSO_4, 5H_2O$.

This value is not found simply by adding the latent heat of evaporation to the figures for the heat of hydration with water vapour, since the latent heat of evaporation given in the tables refers to the *boiling point,* and varies considerably with the temperature.

Then we may suppose the hydration carried out as follows :

(i.) n mols of water *vapour* at temperature T and under dissociation pressure p, are compressed isothermally to the vapour pressure p_0 of pure water. The energy of the vapour is unchanged (assumed an ideal gas, § 33).

(ii.) Condense to liquid water: the increase of energy is $- n\lambda_e + n$RT.

(iii.) Change the pressure of the liquid water from p_0 to p : the energy change is negligible.

(iv.) Bring the liquid water in contact with the solid salt ; let heat Q be absorbed : the work is negligible.

The increase of energy in changes (i.)—(iv.) is $- n\lambda_e + n$RT + Q = [a]. The increase in energy when n mols of water *vapour* are brought *directly* in contact with the salt is $- n\lambda_d +$

$n\mathrm{RT} = [\beta]$. But $[\alpha] = [\beta]$ $\therefore$ $\mathrm{Q} = n(\lambda_e - \lambda_d)$, or if $\mathfrak{Q} = -\mathrm{Q}$ is the heat *evolved* in the hydration of the salt with liquid water :

$$\mathfrak{Q} = n(\lambda_d - \lambda_e) = n\mathrm{RT}^2 . d\ln p/d\mathrm{T} - n\mathrm{RT}^2 . d\ln p_0/d\mathrm{T}$$

$$\mathfrak{Q} = n\mathrm{RT}^2 . d\ln (p/p_0)/d\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad [90]$$

Put $p/p_0 = x$ and integrate [90], assuming $\mathfrak{Q}$ constant

$$\therefore \qquad n \log \frac{x_2}{x_1} = \frac{\mathfrak{Q}}{4{\cdot}576}\left(\frac{1}{\mathrm{T}_1} - \frac{1}{\mathrm{T}_2}\right) \quad . \quad . \quad . \quad . \quad [90a]^1$$

The following results were found in the case of copper sulphate :

$$\mathrm{CuSO_4, 5H_2O} \rightleftharpoons \mathrm{CuSO_4, 3H_2O + 2H_2O},$$

the vapour pressures being determined by passing the same volume of air over the hydrate and then through pure water, and absorbing the moisture from the saturated air in each case.[2]

t° C.	p mm.	p_0 mm.	x.	$\mathfrak{Q}$ calc. per mol liquid water.
25·0	7·92	23·76	0·3334	3,630 (25°—30°)
30·0	11·74	31·83	0·3689	3,290 (30°—35°)
35·0	17·01	42·19	0·4031	3,460 (25°—35°)
			Mean	3,460

Thomsen found $\mathfrak{Q}$ = 3,410 cal. by direct observation ; Frowein, by statical measurements of the pressures, found 3,340 cal. : an error of 0·01 mm. in p affects $\mathfrak{Q}$ by 25 cals.

The measurement of the weight of substance carried away by a current of inert gas may be applied also in the *determination of vapour pressures.* In this way Wartenberg[3] found the vapour pressures of metals and salts at high temperatures. The vapour pressures found with different velocities of the gas are extrapolated to zero velocity. From such results one may calculate the latent heats of evaporation of metals, etc., by [84].

42. Fusion.

—The phenomena of fusion are parallel to those of evaporation : at each pressure there is a definite *melting point,* when liquid and solid are in equilibrium ; $p = f(\mathrm{T})$, and a definite amount of heat, the *latent heat of fusion,* L_f, is absorbed in the transformation of unit mass of solid into liquid.

The changes of volume and the quantities of heat absorbed during fusion are smaller than those accompanying evaporation :

Substance.	$v_l - v_s$.	$v_g - v_l$.	L_f cal.	L_e cal.
Water	− 0·091 c.c.	+ 1673 c.c.	80	538
Acetic acid	+ 0·121 c.c.	+ 385 c.c.	43	97

The suffixes l, s, g refer to liquid, solid and vapour.

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[1] Frowein, *Z. p. C.*, 1887, **1**, 5.

[2] Partington, *C. S.*, 1911, **99**, 466 ; Partington and D. B. Huntingford, *ibid.*, 1923, **123**, 160, where the literature, corrections, and alternative methods are considered ; cf. also Schumb, *J. A. C. S.*, 1923, **45**, 342.

[3] *Z. E.*, 1913, **19**, 482 ; Wartenberg and Albrecht, *Z. E.*, 1921, **27**, 162 ; Wartenberg and Schulz, *Z. E.*, 1921, **27**, 568 ; Wartenberg and Bosse, *ibid.*, 1922, **28**, 384 ; Kröner, *A. P.*, 1913, **40**, 438.

In a few cases (*e.g.*, water) there is expansion on freezing ($v_l < v_s$); in most cases there is contraction ($v_l > v_s$).[1] In all cases L_f is found experimentally to be positive.

Equation (47) applies also to fusion, and in the same way as was used in the deduction of (79) Clausius and Lord Kelvin[2] found:

$$L_f = T(v_l - v_s)\frac{dp}{dT} \quad . \quad . \quad . \quad . \quad . \quad (91)$$

The values of v are those under the actual pressure of the experiment.[3] There are two possible signs for dp/dT, according to the sign of $(v_l - v_s) = \Delta v$. If this is positive ($v_l > v_s$; substance expands on fusion) $dp/dT > 0$, *i.e.*, $dT/dp > 0$, or the melting point is raised by increase of pressure. If Δv is negative ($v_l < v_s$; substance contracts on fusion, as with ordinary ice), $dT/dp < 0$, *i.e.*, the melting point is lowered by increase of pressure. The two cases may be named the *sulphur type* and the *ice type*, respectively.

Example 1.—In the case of water, L_f = 80·04 gm. cal. per gm. = $4{\cdot}2 \times 10^7 \times 80{\cdot}04$ ergs; v_l = 1·000 c.c.; v_s = 1 091 c.c.; T = 273.

If δp = 1 atm. = 1013225 dynes/cm^2., then

$$\delta T = \frac{1013225 \times 273 \times (-0{\cdot}091)}{80{\cdot}04 \times 4{\cdot}2 \times 10^7} = -0{\cdot}0075^\circ \text{ C. per atm.}$$

The first experiments made by Lord Kelvin in 1850[4] showed that $\delta T = -0{\cdot}0072^\circ$ C. per atm., and Dewar (1880) found that this remained constant up to 700 atm. (Cf. Bridgman, p. 65.)

Example 2.—De Visser[5] (1892), in the case of acetic acid found: $\delta T = +\,0{\cdot}02435^\circ$ C. per atm. Now, in this case L_f = 46·42 gm. cal., T = 289·6, $\Delta v = +\,0{\cdot}0001595$ litre per gm. Thus L_f = 46·42/24·22 litre atm.,

$$\delta T = \frac{289{\cdot}6 \times 0{\cdot}0001595 \times 24{\cdot}22}{46{\cdot}42} = +\,0{\cdot}0241^\circ \text{ C. per atm.,}$$

in good agreement with the experimental value.

Similar calculations apply to *allotropic changes*, which take place at a definite temperature (the *transition temperature*) at a given pressure, with the absorption or evolution of a definite amount of heat, L_u per gram.[6]

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[1] Volume changes on fusion: Block, *Z. p. C.*, 1912, **78**, 385, confirms Tammann's formula, $\Delta v = T_0[(\partial v/\partial T)_{p\,\text{liq.}} - (\partial v/\partial T)_{p\,\text{solid.}}]$.

[2] W. Thomson, *P. M.*, 1850, **37**, 123; Clausius, *A. P.*, 1850, **81**, 168.

[3] Richards, *J. A. C. S.*, 1921, **43**, 291.

[4] *P. M.*, 1850, **37**, 123. The lowering of the melting point of ice by pressure was first predicted, from Carnot's principle, by James Thomson in 1849 (*Edin. Phil. Tr.*, 1849, **16**, 54).

[5] *Z. p. C.*, 1892, **9**, 767.

[6] Cohen and Schut, "Piezochemie kondensierter Systeme," 1919, Leipzig.

In the conversion of rhombic to monoclinic sulphur, Reicher[1] (1883) found: $v_{s'} - v_s = +0{\cdot}0000126$ c.c., $L_u = 2{\cdot}52$ gm. cal., $T = 273 + 95{\cdot}6°$, hence $dT/dp = +0{\cdot}045°$ C. per atm. (Obs. 0·05° C. per atm.) The same equation may be applied to the change of the *eutectic point* with pressure; in this case Q is the heat absorbed when 1 gram of the *mixture* fuses.

The experimental data in this field have been greatly advanced by the researches of Tammann,[2] and especially of Bridgman.[3]

Equation (91) may be deduced by a cyclic process, as in § 40. There are now two cases, represented by Figs. 14 and 15.

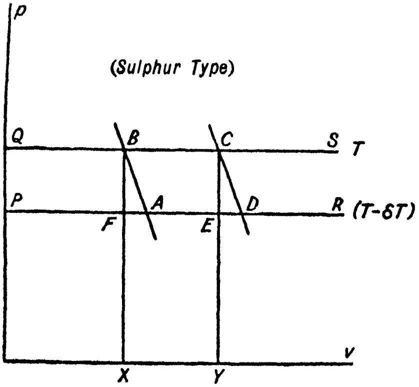

FIG. 14.

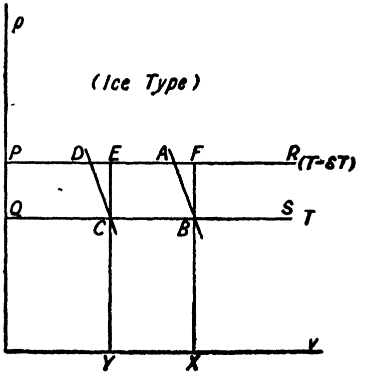

FIG. 15.

A mixture of solid and liquid in equilibrium at temperature $T - \delta T$ under pressure $p - \delta p$ is represented by A. Let PR, QS be the isotherms corresponding with $(T - \delta T)$ and T respectively.

1. The system is compressed (Fig. 14), or expanded (Fig. 15), adiabatically until the temperature rises to T.
2. The cylinder is transferred to the hot reservoir and the system expanded (Fig. 14), or compressed (Fig. 15), until unit mass of solid has liquefied, the heat *absorbed* being L_f.
3. The system is expanded (Fig. 14), or compressed (Fig. 15), adiabatically until the temperature falls to $T - \delta T$.
4. The cylinder is transferred to the cold reservoir and compressed (Fig. 14) or expanded (Fig. 15), until the initial state A is reached from D.

The work done in the cycle is $FB \times BC = dp/dT \,.\, \delta T \,.\, (v_l - v_s)$. The heat absorbed from the hot reservoir is L_f

$$\therefore\ dp/dT.\delta T\,(v_l - v_s) = L_f \times \delta T/T, \text{ by Carnot's theorem,}$$

$$\therefore \frac{dp}{dT} = \frac{L_f}{T(v_l - v_s)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91)$$

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[1] *Z. f. Kristallogr.*, 1884, **8**, 593.

[2] "Kristallisieren und Schmelzen," Leipzig, 1903; *Z. p. C.*, 1913, **82**, 201; *ibid.*, 1913, **85**, 273.

[3] *Proc. Amer. Acad.*, 1911, **47**, 347; *ibid.*, 1912, **47**, 441; *P. R.*, 1914, **3**, 126, 153; *P. R.*, 1915, **6**, 94; *ibid.*, 1916, **7**, 215; Johnston and Adams, *Z. an. C.*, 1911, **72**, 11.

EXAMPLES VII.

1. MacIntosh (1909) found the following figures for the vapour pressure of liquid HI at different temperatures :

743 mm. at – 39·5° C. ; 539 mm. at – 45·8° C.
638 mm. at – 43·0° C. ; 450 mm. at – 49·2° C.

Assuming that $\log_{10}p$ can be written in the form $a + b/T + c \log_{10}T$, calculate the molecular heat of evaporation of liquid HI at the B.P. (– 35·7° C.).

2. The vapour pressures of the alkali metals are given by Kröner (1913) and Gebhardt (1903) as follows in mm. :

°C.	Cs.	K.	Na.
249·5	0·31	0·05	—
307·5	2·26	0·43	—
355·5	6·65	1·51	—
360	—	—	0·32
420	—	—	1·9
520	—	—	12·4

Find the latent heats of evaporation at 307·5° C. for Cs and K, and 420° for Na.

3. Pure I_2 boils at 185·3° C. Ramsay and Young measured the vapour pressures of I_2 over a wide range :

θ (°C.) .	=137·05°	150·70°	160·90°	169·05°	176·00°	182·00° C.
p (mm.) .	=200	300	400	500	600	700

Calculate the vapour pressure at 154° C. and find at what temperature iodine would boil under a pressure of 624 mm.

The density of I_2 at the B.P. is 3·71. Assuming I_2 vapour to be a perfect gas calculate the latent heat of evaporation.

4. The vapour pressures of saturated KCl solutions at different temperatures are :

23·2° C. ...	18·58 cm.	32·21° C. ...	30·28 cm.	41·78° C. ...	50·10 cm.
26·3° ...	22·09 „	35·7° ...	36·50 „	45·11° ...	58·65 „
29·34° ...	25·88 „	38·36° ...	41·79 „	47·89° ...	67·36 „
				51·1° ...	78·6 „

Compare these figures with those obtained from the formulæ proposed by Bertrand, Biot and Regnault, and Kirchhoff. The constants are for saturated KCl solutions :

Bertrand's equation : log A = 7·60807 ; B = 74·99 ; n = 50.
Biot and Regnault : a = 4·88592 ; b = 27·2331 ; α = 0·9932.
Kirchhoff : C = 11·0458 ; B = – 0·85492 ; A = – 2270.

5. Compare the values of the vapour pressures of saturated $Na_2CO_3 10H_2O$ solution obtained from Bertrand's, Biot and Regnault's and Kirchhoff's equations with those obtained experimentally :

t° C.		p in mm.	t° C.		p in mm.
36	...	34·93	46·1	...	60·80
39·14	...	41·54	47·9	...	67·02
41·89	...	48·39	49·95	...	74·35
43·9	...	54·11			

Constants :

Biot and Regnault : a = 5·16043 ; b = 29·7173 ; α = 0·996.
Bertrand : log A = 8·10063 ; B = 80·54.
Kirchhoff : A = – 3052·33 ; B = – 5·14627 ; C = 24·23539.

6. According to Taylor and Smith (1922) the vapour pressure of ether, p, expressed in mm. of Hg is related to the absolute temperature T by the equation:
$\log p = -(2168{\cdot}599/\mathrm{T}) + 13{\cdot}882702 - 0{\cdot}01814165\mathrm{T} + 0{\cdot}00001718195\mathrm{T}^2$
when $\mathrm{T} < 273°$ K.

If the specific volume of ether vapour at − 30° C. = 5515·5 and that of liquid ether at the same temperature = 1·30041, calculate the latent heat of vaporisation of ether at − 30° C.

7. The vapour pressures of liquid ammonia are:

0°.	5°.	10°.	15°.	20° C.
4·19	5·04	6·02	7·14	8·41 atm.

The specific volumes of liquid and gas are:

v_l	1·566	1·582	1·598	1·616	1·634 c.c.
v_g	293·9	245·2	206·0	174·1	148·0 „

Calculate the values of L_e at 5°, 10° and 15°, and compare with the values assuming ideal gas.

8. The dissociation pressures of ammonium hydrosulphide in mm. at various temperatures are (Isambert): 9·5°, 175; 12°, 212; 15°, 259; 18°, 322; 22°, 410; 25·1°, 501. Find the heat of dissociation and compare with the value 22,800 gm. cal. found directly.

($dp/dT = (p_2 - p_1)/(T_2 - T_1)$ for small intervals of temperature; cf. *H. M.*, §§ 68—71).

9. The melting point of *p*-toluidine depends on the pressure according to the relation $t = 45 + a\,(p - 1) - b\,(p - 1)^2$ where t is the M.P. in °C, under a pressure of p atm., $a = 0{\cdot}014215$ and $b = 0{\cdot}0000430$. Calculate the melting-point under a pressure of 7 atmospheres and find at what pressure the M.P. = 45·4°. Find also the latent heat of expansion per unit volume of *p*-toluidine at the M.P.

10. The latent heat of fusion of naphthalene at its normal m. pt., 79·9°, is 35·62 cal. The value of $v_l - v_s$ is + 0·146. Find the change of melting point per atm. and compare with the experimental value 0·0357°.

11. Calculate the heats of hydration of the reactions (Partington and Huntingford):

$CuSO_4, 5H_2O \longrightarrow CuSO_4, 3H_2O$: Vapour pressure at 25°, 7·92 mm.; 30°, 11·74 mm.; 35°, 17·01 mm.

$Na_2HAsO_4, 12H_2O \longrightarrow Na_2HAsO_4, 7H_2O$: Vapour pressure at 25°, 11·10 mm.; 30°, 15·25 mm.; 35°, 20·74 mm.

12. The latent heat of fusion of ice at 0° is 79·77 cal.; the latent heat of supercooled water at − 6·5° C. is 76·03. Find the specific heat of ice.

13. Baxter, Hickey and Holmes give the following vapour pressure measurements with iodine:

55° C.	3·084 mm.	35° C.	0·699 mm.
45° C.	1·498 mm.	25° C.	0·305 mm.

Find the molecular heat of sublimation at 50° C.

14. The melting point of I_2 is 114° C. The increase of vapour pressure per unit increase of temperature at the M.P. is 4·35 mm. Calculate the molecular heat of sublimation of solid I_2 at the M.P., given that the vapour pressure of I_2 at the M.P. is 88·88 mm. of Hg.

15. Calculate the latent heat of sublimation of ice at − 10° from the following vapour pressures: 1·862 mm. at − 10·5°; 1·947 mm. at − 10°; 2·035 mm. at − 9·5°.

16. The vapour pressures of iodine are: 0° C., 0·030 mm.; 15° C., 0·131 mm. 25° C., 0·305 mm. Find the latent heat of sublimation at the M.P. = 114° C.

17. Calculate c_v for mercury given that c_p = 0·0333 at 0° C.; its coefficient of expansion is 0·00018 and its coefficient of compressibility (in atm.) = $0{\cdot}0_5 3$.
Calculate also the increase of pressure required to keep a given volume of mercury constant when it is heated from 0° C. to 1° C.

18. The vapour pressure of propyl alcohol may be represented by the Biot-Regnault formula $\log p = a + b\beta^{t+20} + c\gamma^{t-20}$. The values of the constants are : a = 4·479370, log b = − 0·6084941, log (− c) = 0·5509601, log β = 0·001641423 and log γ = − 0·00342975. Calculate the boiling point of propyl alcohol under normal atmospheric pressure.

19. The following numbers were obtained by Speranski (1912) for the vapour pressure (p) in mm. of saturated $CuCl_2.2H_2O$ solution at the various temperatures (°C.) :

t.		p.	t.		p.
25·0	...	15·97	35·95	...	29·71
28·35	...	19·42	37·8	...	32·75
30·35	...	21·76	38·4	...	33·86

Show that these numbers agree with the second vapour pressure formula due to Bertrand, viz., $p = m. 10^{-n/T}$, m and n being constants.

CHAPTER VIII

The Characteristic Equation

43. The Joule-Thomson Effect.—It has already been stated (§ 33) that Joule's law:

$$(\partial u/\partial v)_{\mathrm{T}} = 0$$

is only very approximately followed by actual gases, and the further investigations of Joule and William Thomson (afterwards Lord Kelvin) gave results which showed the extent to which gases deviated from the ideal state. A stream of gas, under a constant pressure higher than atmospheric, was forced continuously through a porous plug of cotton-wool or silk, supported in a boxwood tube. The temperatures of the gas before and after the plug were determined by thermometers, and after various corrections the change in the temperature of the gas in expanding through the plug was found.[1]

Let p_{A}, v_{A}, $\mathrm{T_A}$, and p_{B}, v_{B}, $\mathrm{T_B}$ be the pressures, specific volumes, and absolute temperatures of the gas before and after passing the plug, respectively (Fig. 16).

We may suppose this transition brought about by passing a volume v_{A} of gas through the plug by means of a piston exposed to the constant pressure p_{A}, and then allowing it to push out, through a volume v_{B} on the other side of the plug, a piston exposed to the constant pressure p_{B}.

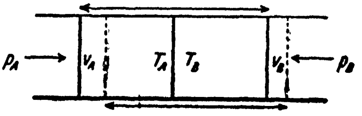

FIG. 16.

If Q is the heat absorbed by unit mass of the gas in passing through the plug, u_{A} and u_{B} its intrinsic energies in the initial and final states, then:

$$\begin{aligned} \mathrm{Q} = \Delta\mathrm{U} + \mathrm{A} &= (u_{\mathrm{B}} - u_{\mathrm{A}}) + (p_{\mathrm{B}}v_{\mathrm{B}} - p_{\mathrm{A}}v_{\mathrm{A}}) \\ &= (u_{\mathrm{B}} + p_{\mathrm{B}}v_{\mathrm{B}}) - (u_{\mathrm{A}} + p_{\mathrm{A}}v_{\mathrm{A}}) = \mathrm{H_B} - \mathrm{H_A}\ (\S\ 20). \end{aligned}$$

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[1] See Preston, "Theory of Heat," for a description of the experiments.

For adiabatic conditions at the plug this vanishes, ∴ H is constant

$$\therefore \quad dH = (\partial H/\partial T)_p dT + (\partial H/\partial p)_T dp = 0$$

$$\therefore \quad (\partial T/\partial p)_H = -(\partial H/\partial p)_T/(\partial H/\partial T)_p$$

∴ from (36), (36a), (32) and (47) :

$$(\partial T/\partial p)_H = [T(\partial v/\partial T)_p - v]/c_p = \frac{T^2}{c_p}\frac{\partial}{\partial T}\left(\frac{v}{T}\right)_p \quad . \quad . \quad (92)$$

giving the heating or cooling effect per unit mass per unit drop of pressure through the plug or expansion valve ; the so-called *Joule-Thomson effect.*

For an ideal gas : $pv = RT/M \quad \therefore \quad T(\partial v/\partial T)_p = RT/Mp = v$

$$\therefore \quad (\partial T/\partial p)_H = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [93]$$

This is satisfied by *any* gas for which :

$$T(\partial v/\partial T)_p - v = 0 \quad \text{or } (\partial v/\partial T)_p = v/T \quad . \quad . \quad (94)$$

Joule and Kelvin's[1] experiments showed that $(\partial T/\partial p)_H$ was fairly small, and almost constant for moderate differences of pressure. In the case of air :

$$\Delta T°C. = 0{\cdot}276(273/T)^2 \times \Delta p \text{ atm.}$$

where T = initial temperature in °K. With other constants, instead of 0·276, similar equations hold for other gases. These equations are only approximate ; the value of $(\partial T/\partial p)_H$ may change sign with alteration of the temperature, and in doing so passes through the value zero, so that equation (94) is the condition for an *inversion point.* We shall return to this later (§ 50).

The *Joule effect,* or the change of temperature of a gas undergoing changes of volume adiabatically without performance of work (§ 33) may be calculated ($du = 0$) :

$$du = \delta Q - \delta A = (c_v dT + l_v dv) - p dv = c_v dT + (l_v - p)dv = 0$$

$$\therefore \quad c_v(\partial T/\partial v)_u = -(l_v - p) \qquad \therefore \text{ from (47) :}$$

$$(\partial T/\partial v)_u = -[T(\partial p/\partial T)_v - p]/c_v = -\frac{T^2}{c_v}\frac{\partial}{\partial T}\left(\frac{p}{T}\right)_v \quad . \quad . \quad (95)$$

$$\text{Thus} \qquad (\partial T/\partial v)_u = 0 \text{ when } (\partial p/\partial T)_v = p/T \quad . \quad . \quad . \quad (95a)$$

Equation (92) gives the correction for the constant pressure gas thermometer; equation (95) for the constant volume gas thermometer. The value of $(\partial T/\partial v)_u$, however, is too small to be measured with accuracy.

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[1] *P. T.*, 1853, **143**, 357 ; 1854, **144**, 321 ; 1862, **152**, 579 ; newer measurements, cf. Jellinek, "Physikal. Chem.," Vol. I., pp. 406 ff. ; Keyes, *J. A. C. S.*, 1921, **43**, 1452 ; Hoxton, *P. R.*, 1919, **13**, 438 (bibliography), finds $(\partial T/\partial p)_H = -0{\cdot}2599 + 182{\cdot}0\frac{1}{T} - 552{\cdot}4\frac{p}{T^2}$ (p in *m.* Hg) for air.

44. **Liquefaction of Gases.**—The fall in temperature produced by the expansion of a gas through a valve, due to the Joule-Thomson effect, is applied in the liquefaction of air and other gases,[1] the fall in temperature being rendered cumulative by passing the cooled expanded gas over metal pipes bringing the compressed gas to the expansion valve. Hydrogen shows a small heating effect on expanding through a valve at the ordinary temperature, but has an inversion point at − 80·5° at 113 atm. pressure. By previously cooling the compressed hydrogen below this temperature it becomes further cooled on expansion and may be liquefied. The inversion temperature of helium is as low as − 240° C. There is also, probably in all cases, a *minimum* temperature at which cooling on expansion takes place. Claude allows the gas, in addition, to perform *external* work by expansion in an engine, and the heat equivalent of this work is taken from the gas.

The observed fall in temperature on expansion is not due to the deviation from Boyle's law, $p_B v_B - p_A v_A$, alone, but includes the Joule effect $u_B - u_A$. For 1 kgm. of air if v is in m.^{3}, p in kgm./m.^{2}, it is known that pv at 1 atm. $=$ 8000 kgm. m., and at 95 atm., 7744 kgm. m. The work done on free expansion from 95 atm. to 1 atm., due to the deviation from Boyle's law, is, therefore, 256 kgm. m. $=$ 0·6 kgm. cal. The maximum fall in temperature due to this cause would be only $0{\cdot}6/c_v = 0{\cdot}6/0{\cdot}17 = 3{\cdot}5°$ C., or 0·036° C. per atm. The fall due to the Joule-Kelvin effect is 0·2732° C. per atm., *i.e.*, eight times as much. At still higher pressures the deviation from Boyle's law is less, since pv is a minimum at 95 atm.

45. **Characteristic Equations.**—The liquefaction of gases by cooling and pressure, and the critical phenomena discovered by Andrews (1869) indicate clearly that the characteristic equation of the ideal gas: $pv = RT$, which gives no account of these important results, may become very unsatisfactory under high pressures. Various alternative characteristic equations have been proposed to account for the observed properties of gases, a description of which will be found in appropriate treatises.[2]

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[1] See Greenwood, "Industrial Gases," 1920; Claude, "Liquid Air, Oxygen, Nitrogen," tr. Cottrell, 1913; *F. S.*, 1922, **18**, 139 ff.

[2] O. E. Meyer, *Kinetic Theory of Gases* (trans. Baynes); Kuenen, *Die Zustandsgleichung der Gasen* (1907); Boltzmann, *Vorlesungen über Gastheorie*, 2 vols., 1896–98; Jeans, *Dynamical Theory of Gases*, 3rd edit., 1921; van der Waals, *Die Kontinuität*, Leipzig, 1881; van der Waals and Kohnstamm, *Lehrbuch der Thermodynamik*, vol. 1, 1908; Kamerlingh Onnes and Keesom, *Die Zustandsgleichung*, Enzyklop. Math. Wiss., V., 1912; Jellinek, *Lehrbuch der physikalischen*

The first attempt to correct the ideal gas equation was made by Hirn (1867), who wrote:

$$p(v - b) = \mathrm{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (96)$$

where b is a constant, called the *co-volume*.[1]

A further correction was introduced by van der Waals (1873), and his famous equation:

$$(p + a/v^2)(v - b) = \mathrm{RT} \quad . \quad . \quad . \quad . \quad . \quad (97)$$

where a is a second constant, represented a great advance.

If in (97) we put $v =$ const., then $p = \mathrm{BT} - \mathrm{A}$, where A and B are constants. If p and T are plotted at constant volume the curves (*isochores*) should be straight lines. This has been confirmed by extensive experiments with ether by Ramsay and Young.[2]

Subsequent characteristic equations have mainly introduced modifications of van der Waals' equation to take account of the undoubted variation of a and b with temperature and pressure.

Only one of these will be considered in detail, viz., that of D. Berthelot[3]:

$$(p + a/\mathrm{T}v^2)(v - b) = \mathrm{RT} \quad . \quad . \quad . \quad . \quad . \quad (98)$$

where a in van der Waals' equation is replaced by a/T (a is a new constant). For gases under relatively small pressures (up to 5 atm.) this gives very accurate results.

The values of a and b depend on the units of pressure and volume and on the mass of gas. If p is in atm., v in c.c. per mol, then $\mathrm{R} = 82{\cdot}07$ c.c. atm./1° C. According to van der Waals, the value of b is equal to four times the actual volume of the molecules in the volume v; according to O. E. Meyer, the multiple is $4\sqrt{2}$, and this is apparently in better agreement with experiment. Van Laar believes that b is the actual volume occupied by the molecules.[4]

Chemie, vols. 1 and 2; Nernst, *Theoretische Chemie*, 8th edit., 1921; Jaeger, *Fortschritte der kinetischen Gastheorie*, 1906; Mathias, *Le point critique des corps purs*, Paris, 1904; Andrews, *Scientific Papers*, London, 1889; Amagat, *Notes sur la physique et la thermodynamique*, Paris, 1912; *ibid.*, *Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux très hautes pressions*, Paris, 1893; A. W. Porter, *P. M.*, 1906, **11**, 554; 1910, **19**, 888, and subsequent papers; Boynton and Bramley, *P. R.*, 1922, **22**, 46.

[1] Berthelot, *C. R.*, 1900, **130**, 115.

[2] *P. M.*, 1887, **23**, 435. See Fitzgerald, *P. R. S.*, 1887, **42**, 50.

[3] *Sur les thermomètres à gaz, Trav. et Mém. du Bureau Internat. des Poids et Mésures*, 1907, vol. 13; Nernst, *loc. cit.*

[4] Quoted by Young, "Stoichiometry" 1918, p. 186.

46. The Critical Constants.—One of the most important advances represented by van der Waals' equation is its ability to give a good account, on quantitative lines, of liquefaction and critical phenomena.

Equation (97), written in the form of a cubic equation in v:

$$v^3 - v^2 (\mathrm{R}\mathrm{T}/p + b) + v \,.\, a/p - ab/p = 0 \quad . \quad . \; (97a)$$

will, for every pair of values of p and T, give *three* values of v. The theory of equations shows that these roots are either: (i.) all real, or (ii.) one real and two imaginary. The physical interpretation is that, according to the conditions of temperature and pressure, a fluid can exist either in *three* distinct states with definite specific volumes, or in only *one* state (imaginary roots having no physical significance). In the first case the smallest value of v corresponds with the liquid, and the largest with the gas; the exact interpretation of the intermediate value is difficult, but the graphical consideration below indicates that it is unstable. The second case, where only one real value of v exists, may be supposed to apply to a substance above its critical temperature.

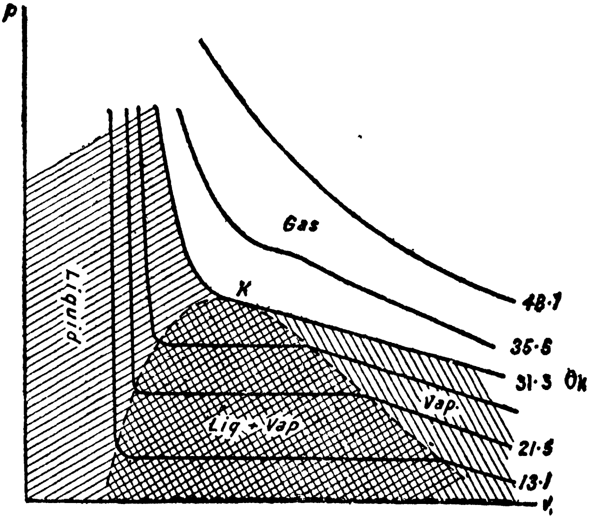

FIG. 17.

These relations are most clearly seen by a comparison of the actual liquefaction curves found by Andrews (1863)[1] for carbon dioxide (Fig. 17) with a series of theoretical isotherms obtained by plotting corresponding values of v and p for different values of T by van der Waals' equation (Fig. 18).

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[1] *P. T.*, 1876, **166**, 421; 1869, 575; "Scientific Papers," 1889, 296; Mathias, "Le point critique des corps purs," Paris, 1904.

Fig. 17 shows the isotherms for various temperatures, for the same amount of carbon dioxide. Below 31·3°, starting on the right, liquefaction begins at a definite pressure for each temperature, and the curve than becomes horizontal, the pressure being constant as long as two phases (gas and liquid) are present. When all is liquid the curve turns sharply and steeply upwards, since the liquid is only slightly compressible. When the curves are traced at higher temperatures, the two ends of the horizontal line, representing coexistence of liquid and gas, approach, and at 31·3° the isotherm no longer shows any horizontal *interval,* but passes through a *point of inflexion* at a pressure of 75 atm. At the same time no appearance of liquefaction can be observed in the tube in which the gas is compressed. Above 31·3° the isotherms gradually approach a hyperbolic form (pv = const.).

There is, for every gas or vapour, a definite temperature above which the substance cannot be liquefied by pressure alone. This is called the critical temperatrue (θ_c, or T_c).[1]

The critical temperature is the highest temperature at which a gas may be liquefied by pressure, and the highest pressure which produces liquefaction is called the *critical pressure,* p_c. It is given by the ordinate of the point of inflexion on the *critical isotherm* (31·3° in the case considered), *i.e.*, the ordinate of the *critical point,* K.

The specific volume of the substance under the critical pressure and at the critical temperature is called the *critical volume,* v_c. (Another definition of the critical volume is sometimes employed, viz., the ratio of the volume of the substance in the critical state to the volume of a gas at 0° C. and 760 mm.)

A *condition for the critical state* is seen from the diagram to be that the p, v isotherm shall exhibit a *point of inflexion.* Such is the case [2] when :

$$(\partial p/\partial v)_T = 0 \text{ and } (\partial^2 p/\partial v^2)_T = 0 \quad . \quad . \quad . \quad . \quad (99)$$

Thus, the compressibility at the critical point is $-\infty$

The values of these coefficients may be calculated from the characteristic equation.

In Fig. 18 a theoretical isotherm is plotted from van der Waals' equation, below the critical temperature. The *real isotherm* is formed of the left and right portions and the horizontal *ac*; the isotherm plotted from the equation is *adec*, cutting *ac* in three points, *a*, *b* and *c*, for a particular temperature and pressure. $a(v_a)$ is the volume of the liquid, $c(v_c)$, that of the gas, and the volume, v_b, corresponding with *b*, is an unstable intermediate homogeneous state, which lies on a hypothetical part of the isotherm *de*, along which the pressure would increase with the volume.[1] The extrapolated portions *ad* and *ce* represent superheated liquid, and supercooled vapour, respectively, and are attainable. On the critical isotherm the points *a*, *b*, and *c* will have coalesced to the point of inflexion :

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[1] There is no experimental evidence of the existence of a critical point of fusion when liquid and solid would become identical (Tammann, " Kristallisieren und Schmelzen," 1903 ; *A. P.*, 1911, **36**, 1027).

[2] See *H. M.*, § 27 ; dy/dx undergoes no change of sign in passing through the point of inflexion, hence $d^2y/dx^2 = 0$.

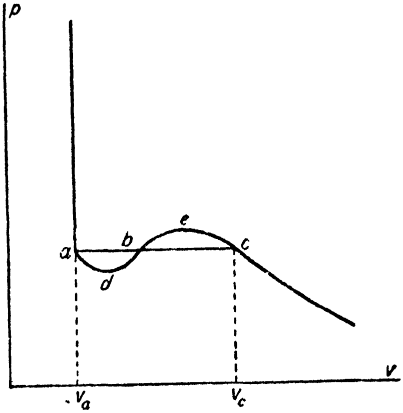

FIG. 18.

$$v_a = v_b = v_c = \text{critical volume} = v_c.$$

From (97) in the form $p + a/v^2 = RT/(v - b)$, and (99), we find at the critical point :

$$(\partial p/\partial v)_T = 2a/v_c^3 - RT_c/(v_c - b)^2 = 0 \quad \therefore 2a/v_c^3 = RT_c/(v_c - b)^2;$$

$$(\partial^2 p/\partial v^2)_T = -6a/v_c^4 + 2RT_c/(v_c - b)^3 = 0$$

$$\therefore \quad 6a/v_c^4 = 2RT_c/(v_c - b)^3.$$

$$\text{By division: } v_c/3 = v_c/2 - b/2 \quad \therefore v_c = 3b$$

$$\therefore \quad 2a/(3b)^3 = RT_c/(2b)^2$$

$$\therefore \quad T_c = 1/R.8a/27b, \text{ and from (97) } p_c = a/27b^2$$

$$\therefore \quad v_c = 3b;\ p_c = a/27b^2;\ T_c = 1/R\,.\,8a/27b \quad . \quad . \quad (100)$$

$$\text{or} \quad a = 3p_cv_c^2;\ b = v_c/3;\ R = 8p_cv_c/3T_c. \quad . \quad . \quad (100a)$$

Thus, from the compressibility (*a*, and *b*) the critical constants may be calculated,[2] and *vice versâ*. With 1 gm. of substance, *p* in atm. and *v* in c.c., the unit of *b* is $\text{cm.}^3/\text{gm.}$; and of *a* $\text{atm. cm.}^6/\text{gm.}^2$

47. Theory of Corresponding States.[3]—Let the values of

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[1] Cf. J. Meyer, *Z. E.*, 1912, **18**, 709.

[2] Guye and Friedrich, *A. G.*, 1905, **19**, 505; Häntzschel, *A. P.*, 1905, **16**, 565; Kuenen, *ibid.*, 1905, **17**, 189.

[3] Van der Waals; cf. Kleeman, *P. M.*, 1912 [vi.], **24**, 391; also Kaufmann, *P. M.*, 1915, [vi.], **30**, 146.

p, v and T in (97) be expressed as fractions of the critical values:

$$\left.\begin{aligned} p &= \pi p_c;\ v = \phi v_c;\ \mathrm{T} = \vartheta \mathrm{T}_c \\ \text{or}\quad \pi &= p/p_c;\ \phi = v/v_c;\ \vartheta = \mathrm{T}/\mathrm{T}_c \end{aligned}\right\} \quad . \quad . \quad . \quad (101)$$

π, ϕ, and ϑ are known as the *reduced pressure, reduced volume,* and *reduced temperature,* respectively. Then:

$$(\pi p_c + a/\phi^2 v_c^2)(\phi v_c - b) = \mathrm{R}\vartheta\mathrm{T}_c$$

$$\therefore \text{ from (100)} \quad (\pi + 3/\phi^2)(3\phi - 1) = 8\vartheta \quad . \quad . \quad . \quad . \quad . \quad (102)$$

All characteristic constants (a, b, R) have now vanished, and the equation is true for *any substance,* provided no change of molecular complexity occurs over the range of temperature and pressure considered.

Equation (102) is known as a *reduced equation.* Any states of substances characterised by the same values of π, ϕ and ϑ are called *corresponding states.*

Many other equations than (97) lead to laws of corresponding states, although the exact form of equation corresponding with (102) varies from case to case. The general expression of the *law of corresponding states* is that all substances should behave alike for the same values of π, ϕ and ϑ. This is approximately true.

The most general form of characteristic equation is

$$\mathrm{F}(p, v, \mathrm{T}, c_1, c_2, c_3, \ldots) = 0 \quad . \quad . \quad . \quad . \quad (103)$$

where c_1, c_2, . . . are constants characteristic of the particular substance, including the molecular weight, since R is the same only for equimolecular amounts. At the critical point the two equations (99) enable us to express three constants in (103) in terms of the critical data. If the resulting equation is a reduced equation, it must contain no constants characteristic of the substance, hence (103) can contain only *three* such constants. In this case it can always be written in the form:

$$f(p, v, \mathrm{T}, p_c, v_c, \mathrm{T}_c) = 0$$

and since it is to be independent of the units adopted, it must be of the form $f(p/p_c, v/v_c, \mathrm{T}/\mathrm{T}_c)$, or

$$f(\pi, \phi, \vartheta) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (104)$$

An equation of state, therefore, leads to a law of corresponding states when it contains only three characteristic constants, and exhibits a critical point.[1] Equations containing more than three constants (*e.g.*, Clausius's and Wohl's) take account of deviations from the law of corresponding states.

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[1] **Meslin, *C.R.*, 1893, 116, 135; cf. Kaufmann, *P. M.*, 1915, 30, 146.**

Experiments to test the law of corresponding states have been made by Amagat (1896) and Raveau (1897).[1] Raveau plotted the logarithms of the pressures and volumes for various substances:

$$\log \phi = \log v - \log v_c = \log v - \textit{const.}$$

and similarly, $\log p/p_c = \log p - \textit{const.} = \log \pi$.

The values of $\log \phi$ and $\log \pi$ were plotted from (102) for various values of ϑ. The observed values of $\log p$ and $\log v$ were then plotted on a translucent sheet of paper and this laid over the preceding sheet of curves. Since the reduction of $\log p$ to $\log \pi$, and of $\log v$ to $\log \phi$, requires merely the addition of a constant, it should be possible to bring the two sets of curves into coincidence merely by shifting one sheet over the other parallel to the axes of p and v. The critical point was brought into coincidence, and it was then found that the two sets of curves did *not* coincide, but cut one another. The reduced van der Waals' equation is not, therefore, accurate. The very careful experiments of Young have shown that even the law of corresponding states itself is not rigorously true.[2]

Another method of testing the theory of corresponding states, deduced from van der Waals' equation, was used by Young (1900).[3] The equation (100a) gives:

$$\mathrm{RT}_c/p_c v_c = 8/3 = 2{\cdot}67.$$

If p_c is in atmospheres, v_c in c.c. per gram, then $\mathrm{R} = 82{\cdot}1/\mathrm{M}$, and if $\rho_c = 1/v_c$ = density in grams per c.c., then:

$$\mathrm{RT}_c/p_c v_c = \frac{82{\cdot}1}{\mathrm{M}} \cdot \frac{\rho_c \mathrm{T}_c}{p_c} = 2{\cdot}67$$[*]

D. Berthelot (equation 129a) puts $\mathrm{RT}_c/p_c v_c = 32/9 = 3{\cdot}56$. The observed value was found to be 3·75 (15/4) for most substances; for argon it is 3·424, for oxygen, 3·419, for nitrogen 3·421, for xenon 3·605.[†] Van der Waals' equation again fails.

Another method has been used by A. W. Porter,[4] in which the

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[1] Amagat, *C. R.*, 1896, **123**, 30, 83; *J. P.*, 1897, **6**, 1; "Notes sur la thermodynamique," pp. 38 ff.; Raveau, *C. R.*, 1896, **123**, 100; *J. P.*, 1897, **6**, 432; K. Meyer, *Z. p. C.*, 1900, **32**, 1; D. Berthelot, *C. R.*, 1900, **130**, 565, 713; **131**, 175; *J. P.*, 1901, **10**, 611; Kamerlingh Onnes, *A. N.*, 1897, **30**, 101; Jellinek, "Physik. Chem.," vol. 2, pp. 65 ff.; Byk, *P. Z.*, 1921, **22**, 15.

[2] Young, "Stoichiometry," 1918, p. 220; cf. K. Meyer, *Z. p. C.*, 1900, **32**, 1.

[3] *P. M.*, 1900, **50**, 291.

[*] See P. Walden, *Z. p. C.*, 1909, **66**, 437.

[†] See "Dictionary of Applied Physics," London, 1922, Vol. I., p. 891; Kleeman, *P. M.*, 1909, **18**, 905.

[4] *P. M.*, 1906, **11**, 554; *P. R. S.*, 1914, **89**, 377.

inversion point of the Joule-Thomson effect is applied. Equation (94) gives, in terms of reduced magnitudes:

$$\vartheta\left(\frac{\partial\phi}{\partial\vartheta}\right)_\pi - \phi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (105)$$

If we now differentiate (102) with respect to ϑ (π const.) and substitute from (105) we find:

$$-\frac{8\vartheta}{3\phi - 1} + \frac{6(3\phi - 1)}{\phi^2} = 0$$

$\therefore$ at the inversion point:

$$\vartheta = \frac{3(3\phi - 1)^2}{4\phi^2}.$$

Eliminate ϑ $\quad\therefore\quad \pi = 9(2\phi - 1)/\phi^2$

For all pressures from 0 to $9p_c$ this equation has two real roots, hence there are *two* inversion temperatures within this region, which may range from a little below, to 6·7 times, the critical temperature. At pressures higher than $9p_c$ there is no inversion point. The experimental results of the compressibilities of carbon dioxide and nitrous oxide gave identical inversion curves, agreeing with the general law of corresponding states, but this was not the curve predicted by van der Waals' equation.

If we assume $v = v_0 = b$ when $T = 0$, then from the relation $v_c = 3b$ deduced from van der Waals' equation we find $v_c/v_0 = 3$. The value of this ratio may be calculated from an empirical relation discovered by Cailletet and Mathias (1886), known as the *law of rectilinear diameter*.[1] If ρ_l and ρ_g are the densities of the liquid and saturated vapour in equilibrium with it, then it is found that $(\rho_l + \rho_g)/2$ is a linear function of temperature. If ρ_l and ρ_g are plotted against temperature, the locus of the points dividing equally the joins of ρ_l and ρ_g is a straight line (Fig. 19):

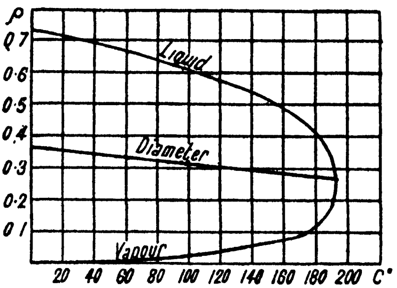

FIG. 19.

$$\tfrac{1}{2}(\rho_l + \rho_g) = \rho_0 + a\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (106)$$

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[1] *C. R.*, 1886, **102**, 1202; 1887, **104**, 1563; Young, *P. M.*, 1900, **50**, 291; Jellinek, "Phys. Chem.," I., 479; von Jüptner, *Z. p. C.*, 1912, **80**, 299; 1913, **85**, 1. This line is not always accurately straight.

where ρ_0 is the mean density of liquid and vapour at 0° C. At the critical temperature $\rho_l = \rho_0 + a\theta_c$. If the line is extrapolated to $T = 0$, the value of ρ will be half the density of the liquid at absolute zero, since the density of the vapour is then zero. In this way it is found that v_c/v_0 is not 3, but varies from 3·6 to 4. Berthelot's equation (§ 51) gives $v_c/v_0 = 4$, in better agreement.[1]

48. **Maxwell's Rule.**—The theoretical isotherm *adec* (Fig. 18, § 46) given by van der Waals' or other characteristic equation leads to three values of v for a given pair of values of p and T (§ 46). The *actual* isotherm is represented by the two ends characteristic of homogeneous liquid and vapour, and the flat portion, *abc*, where two phases are present, *i.e.*, a heterogeneous system.

If we suppose the substance carried round a complete isothermal cycle *adbeca*, the work done is zero, by (44), $\therefore$ work = area of loop $= -$ (area *adb*) + (area *bec*) $= 0$ $\therefore$ area *abd* = area *bec*. Hence *ac*, the line of heterogeneous states, must cut the theoretical isotherm so as to intercept equal areas above and below. This result, which fixes the position of *ac* on each isotherm, was first obtained by Maxwell.[2]

It is not wholly certain, since the part *de* of the cycle represents unstable states.[3]

49. **Vapour Pressures.**—The characteristic equation applies to homogeneous states only, but Maxwell's rule (§ 48) extends its application to the heterogeneous system of liquid in equilibrium with vapour.

Suppose the system carried from the state *a* to the state *c* (Fig. 18, § 46), (i.) along the theoretical isotherm, *adbec* (system homogeneous); (ii.) along the real isotherm, *ac* (system heterogeneous, and pressure constant = P, say). The two amounts of work are equal, since the temperature is constant:

$$\therefore \int_{v_l}^{v_g} p\,dv = \mathrm{P}(v_g - v_l) \quad . \quad . \quad . \quad . \quad . \quad (107)$$

$$\therefore \int_{\phi_l}^{\phi_g} \pi\,d\phi = \pi_{\mathrm{V}}(\phi_g - \phi_l) \quad . \quad . \quad . \quad . \quad (107a)$$

where π_{V} is the reduced vapour pressure, P/p_c.

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[1] R. Lorenz, *Z. an. C.*, 1916, **94**, 240; H. Davies, *P. M.*, 1912 [vi.], **24**, 415; Gay, *C. R.*, 1914, **158**, 34.

[2] *Nature*, 1875, **11**, 357.

[3] Cf. Bryan, "Thermodynamics," 1907, pp. 142 ff.; Amagat, "Notes sur la physique," p. 71.

If the value of π from the reduced characteristic equation is introduced into the integral of (107a), we obtain on integration:

$$f(\pi_v, \phi_l, \phi_g, \vartheta) = 0 \quad . \quad . \quad . \quad . \quad . \quad (108)$$

If the reduced characteristic equation is applied to the liquid alone, and to the vapour alone, we obtain two further equations:

$$f(\pi_v, \phi_l, \vartheta) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (109)$$

$$f(\pi_v, \phi_g, \vartheta) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (110)$$

From these three equations the values of π_v, ϕ_l, ϕ_g can be determined as functions of the reduced temperature:

$$\pi_v = f_1(\vartheta)\ ;\ \phi_g = f_2(\vartheta)\ ;\ \phi_l = f_3(\vartheta) \quad . \quad . \quad . \quad (111)$$

Thus, the reduced vapour pressure, and the reduced volumes of the liquid and vapour, must be the same for all substances at the same reduced temperature.[1]

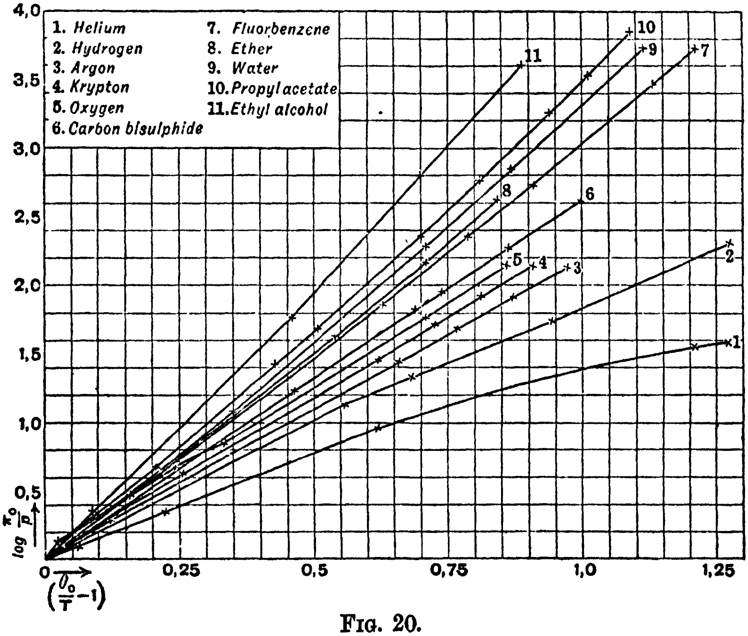

FIG. 20.

(From Nernst's "Theoretical Chemistry," by permission of Messrs. Macmillan.)

A large number of experiments made by Young[2] showed that this was very nearly, but not exactly, the case for normal liquids, whilst "associated" liquids deviated very considerably.

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[1] J. P. Dalton, *P. M.*, 1907, **13**, 517.

[2] Summary in Jellinek, "Phys. Chem.," II., 79 ff.

The result that the reduced vapour pressure curves, $\pi_V = f_1(\vartheta)$, should coincide for all normal substances was tested by Bingham[1] (1906) by plotting $\log p_c/P$ against $(T_c/T - 1)$. The result (Fig. 20) showed that the curves actually deviate more and more as T approaches zero. Substances may, apparently, be divided into three groups: (i.) those of small molecular complexity and low critical temperatures; hydrogen and helium; (ii.) normal substances, such as benzene and ether; (iii.) "associated" substances, such as water and alcohol. Van der Waals had proposed[2] an empirical vapour pressure equation:

$$\log p_c/P = a\,(T_c/T - 1) \quad . \quad . \quad . \quad . \quad (112)$$

where a is a constant, very nearly equal to 3·0.[3] The above curves show that a varies slightly from one substance to another, and (since the curves are not straight lines) the equation is only approximately true.

The reduced Clapeyron-Clausius' equation[4] (91) is:

$$\frac{\lambda_e}{T} = \frac{p_c v_c}{T_c}\left(\frac{d\pi}{d\vartheta}\right)(\phi_g - \phi_l) \quad . \quad . \quad . \quad . \quad . \quad (113)$$

But $p_c v_c/T_c = 3R/8$ according to van der Waals (100a), or $9R/32$ according to Berthelot (129c), hence, *at corresponding temperatures*, λ_e/T should be the same for all substances. According to Guldberg[5] (1890) the boiling points under atmospheric pressure are approximately two-thirds of the critical temperatures, hence, if T_0 is the boiling point, λ_e/T_0 should be the same for all substances. This is (incorrectly) known as *Trouton's rule*.[6] The value of λ_e/T_0 is approximately 21 for normal substances. If, however, the values from van der Waals' equation are substituted in (113) the value of λ_e/T_0 is found to be only 10·8.

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[1] *J. A. C. S.*, 1906, **28**, 723; cf. Nernst, "Theoret. Chem.," 8–10 Aufl., 313, 247.

[2] "Kontinuität," p. 147 (2nd edit.).

[3] Guye, *A. G.*, 1894, **31**, 463, for a series of substances finds a mean value of 3·06. It is larger (3·2) for associated liquids.

[4] Kleeman, *P. M.*, 1909, **18**, 508, deduces the equation $\lambda/T = -R + \frac{\vartheta}{\pi} \cdot \frac{d\pi}{d\theta}$. See also W. C. M. Lewis, *Z. p. C.*, 1912, **78**, 24; **79**, 185, 196.

[5] *Z. p. C.*, 1890, **5**, 374. Thorpe and Rücker, *C. S.*, 1884, **45**, 135, showed that the critical temperature could be calculated from the densities at two temperatures by the formula $T_c = (T_2\rho_1 - T_1\rho_2)/A(\rho_1 - \rho_2)$ where $A = 1{\cdot}974$; cf. Herz, *Z. p. C.*, 1921, **97**, 376. Kurbatoff, for carbon compounds containing more than five carbon atoms, finds that T_0/T_c has a mean value of 0·666. In homologous series it varies from 0·58 for the initial members to 0·70 for the final members. In the case of helium it is 0·998.

[6] It was put forward by Despretz in 1823, by Pictet in 1876, by Ramsay in 1877, and by Trouton in 1884. Kurbatoff (*Beibl. Wied. Ann.*, 1904, **28**, 967), finds the mean value of the ratio λ/T_0 to be 20·7 ± 0·8. Cf. Guye, *A. G.*, 1894, **31**, 164, 463; Estreicher, *P. M.*, 1895, **40**, 454; Louginine, *A. C. P.*, 1898, **13**, 289; *A. G.*, 1900, **9**, 5; *C. R.*, 1901, **132**, 88; Berthelot, *A. C. P.*, 1895, **4**, 133; *C. R.*, 1915, **160**, 657; Traube, *B.*, 1898, **31**, 1562; Crompton, *P. C. S.*, 1901, **17**,

Nernst[1] has proposed two modifications of Trouton's rule:

$$\lambda_e/T_0 = 9{\cdot}5 \log T_0 - 0{\cdot}007T_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (114)$$

$$\lambda_e/T_0 = 8{\cdot}5 \log T_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (115)$$

Bingham[2] has proposed $\lambda_e/T_0 = 17 + 0{\cdot}011T_0$ . . . . (116)

By analogy with Trouton's rule we should expect the quotients of the molecular heats of sublimation, and of dissociation, by the absolute temperatures at which the pressures are equal to 1 atmosphere, to be constant. De Forcrand[3] found this very nearly true; the values are 30 and 32, respectively. Nernst[4] has proposed a modified rule for the dissociation of carbonates:

$$\lambda_d/T_0 = 4{\cdot}571\,(1{\cdot}75 \log T_0 + 3{\cdot}2) \quad . \quad . \quad . \quad (117)$$

Within a fairly wide range of temperature this gives the value 32.

According to Guye[5] the *critical coefficient*, $K = T_c/p_c$, is related to the *molecular refractive power* $MR = M(n^2 - 1)/(n^2 + 2)\rho$, by the equation $K = MR/1{\cdot}8$, and $\therefore p_c = 1{\cdot}8T_c/MR$. For a compound K is the sum of the K's of the component atoms, augmented in certain cases by coefficients depending on the mode of linkage.

Dutoit and Friederich[6] give the formulæ: (1) $p_c = 11{\cdot}1\,[\sigma(Mv)^{\frac{2}{3}}]/Mv$, where $\sigma(Mv)^{\frac{2}{3}}$ = molecular surface energy (§ 105), and v = specific volume at the boiling point (T_0); (2) $p_c = (T_0/Mv).(13{\cdot}8 + Mv/100)$. The first was tested by Guye and Baud.[7] Mathias[8] has pointed out relations between

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61; Kendall, *M. K. N.*, 1913, **2**, No. 36; Pagliani, *G.*, 1916, **46**, ii., 310; Arrhenius, *M. K. N.*, 1911, **2**, No. 8; 1915, **3**, No. 6; Lundén, *ibid.*, 1912, **2**, No. 16; Forcrand, *C. R.*, 1913, **156**, 1439, 1648; Herz, *Z. an. C.*, 1916, **952**, 253.

[1] Cf. "Theor. Chem.," 8–10 Aufl., 313.

[2] *J. A. C. S.*, 1906, **28**, 717; Mali, *P. M.*, 1923, **45**, 94.

[3] *A. C. P.*, 1903, **28**, 384, 531; **29**, 5.

[4] "Theoret. Chem.," 8–10 aufl., p. 802; cf. Martignon, *C. R.*, 1899, **128**, 103. (On Trouton's rule cf. § 122; Pagliani, *N. C.*, 1916, **11**, i., 118; Herz, *Z. an. C.*, 1916, **95**, 253; Cederberg, "Thermodyn. Berechnung chem. Affinitäten," Berlin, 1916.)

Hildebrand (*J. A. C. S.*, 1915, **37**, 970) finds equal values of λ_e/T at temperatures for which the vapour concentrations are equal: for 0·005 mol/litre, the ratio is about 27·5 for normal liquids; 32·4 for NH_3; 32·0 for H_2O.

Winternitz (*P. Z.*, 1914, **15**, 397) calculates the values λ_e/T_0 for H_2 as 15·0, and for tungsten as 41·0; Nernst's formula gives 17·0 and 42·2; these are cases of very low and very high temperatures, where Trouton's rule breaks down.

For a relation between boiling points and critical temperatures of homologous compounds, see Ferguson, *P. M.*, 1915, **29**, 599.

[5] *J. P.*, 1890, **9**, 312.

[6] *A. de G.*, 1900, **9**, 105.

[7] *Ibid.*, 1901, **11**, 449, 537.

[8] "Le Point critique," p. 161.

the critical pressures in homologous series. The writer[1] has suggested the empirical equation : $n = 0{\cdot}642 + 0{\cdot}00116p_c + 0{\cdot}0000399p_c^2$, where n is the exponent in the formula $\eta_T = \eta_0(T/273)^n$ connecting the viscosity (η) of a gas with temperature. (In all cases p_c is in atm.)

An approximate value of ρ_c is one-third the density of the liquid at the lowest possible temperature.[2] Another approximate formula[3] is $\rho_c = (\rho_l + \rho_g)/2(2 - \vartheta)$ (cf. 106), where $\vartheta = T/T_c$. The values of ρ_g may be found by multiplying the theoretical (gas law) densities by the factor k for the corresponding reduced temperature (ϑ) determined by Young[4]: $k =$ actual density/ideal density :

ϑ.		k.	ϑ.		k.
0·57	...	1·005	0·69	...	1·065
0·60	...	1·011	0·71	...	1·082
0·65	...	1·035	0·73	...	1·102
0·67	...	1·050	0·74	...	1·115

Natanson[5] gives $\rho_c = 0{\cdot}044\ p_c/T_c$. (Other methods, cf. Mathias, *loc. cit.*)

50. Thermal Coefficients from van der Waals' Equation.

—For two temperatures at constant volume :

$$(p_0 + a/v^2)(v - b) = RT_0 \text{ and } (p_1 + a/v^2)(v - b) = RT_1$$

$$\therefore\ (p_1 - p_0)(v - b) = R(T_1 - T_0)$$

$$\therefore\quad \beta \equiv (p_1 - p_0)/p_0(T_1 - T_0) = (1 + a/p_0v^2)/T_0 \quad . \quad (118)$$

independent of T, but depending on the density, and greater than the value $1/T_0$ for an ideal gas. Actually, β decreases slightly with rise of temperature.

For two temperatures at constant pressure :

$$(p + a/v_0^2)(v_0 - b) = RT_0 \text{ and } (p + a/v_1^2)(v_1 - b) = RT_1.$$

Subtract and neglect terms in ab, of the second order

$$\therefore\quad p(v_1 - v_0) + a(1/v_1 - 1/v_0) = R(T_1 - T_0).$$

Divide this by the first equation and neglect terms of the second order :

$$a \equiv (v_1 - v_0)/v_0(T_1 - T_0)$$

$$= \frac{1}{T_0}\left\{1 + \frac{a}{pv_0}\left(\frac{1}{v_0} + \frac{1}{v_1}\right) - \frac{b}{v_0}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (119)$$

dependent on pressure and density, or on one of these and temperature.

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[1] Partington, *F. S.*, 1922, **17**, 734.
[2] Mathias, *Ann. Fac. des Sci. de Toulouse*, 1892, **6**.
[3] Mathias, " Le Point critique," p. 164.
[4] *P. M.*, 1892, **33**, 153.
[5] *J. P.*, 1895, **4**, 219.

From an experimental value of β, (118) gives a; from this and an experimental value of α, (119) gives b.

If we write van der Waals' equation in the form:

$$p = \mathrm{RT}/(v - b) - a/v^2$$

differentiation gives: $(\partial p/\partial v)_{\mathrm{T}} = -\mathrm{RT}/(v-b)^2 + 2a/v^3$

$$\therefore (\S\,17) \qquad \epsilon_{\mathrm{T}} = (\mathrm{RT} - 2a/v)/(v - 2b) \quad . \quad . \quad . \quad . \quad (120)$$

Also $(\partial p/\partial \mathrm{T})_v = \mathrm{R}/(v-b) \quad \therefore \quad (\partial p/\partial \mathrm{T})_v = (p + a/v^2)/\mathrm{T}$

$$\therefore \text{ from (95)}: \qquad (\partial \mathrm{T}/\partial v)_u = -\frac{1}{c_v}\cdot\frac{a}{v^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (121)$$

$$\therefore \qquad \mathrm{T}_1 - \mathrm{T}_2 = \int_{v_1}^{v_2} (\partial \mathrm{T}/\partial v)_u dv = \frac{a}{c_v}\left(\frac{1}{v_1} - \frac{1}{v_2}\right) \quad . \quad . \quad (122)$$

giving the Joule effect.

$$\left.\begin{array}{l}\text{Also}: \mathrm{C}_p - \mathrm{C}_v = \mathrm{T}(\partial p/\partial \mathrm{T})_v \,.\, (\partial v/\partial \mathrm{T})_p = \mathrm{R}(1 + 2a/\mathrm{RT}v) \\ = \mathrm{R} + 2ap/\mathrm{RT}^2 \text{ when } a \text{ and } b \text{ are small.}^1\end{array}\right\}. \quad (123)$$

Write (97) in the form:

$$v - b = \mathrm{RT}/p - a/pv + ab/pv^2$$

and substitute $v = \mathrm{RT}/p$ *in the correction terms:*

$$v = \mathrm{RT}/p - a/\mathrm{RT} + abp/\mathrm{R}^2\mathrm{T}^2 + b.$$

Differentiate with respect to T and substitute in (92):

$$\therefore\ d\mathrm{T} = \left(\frac{2a}{\mathrm{RT}} - \frac{3abp}{\mathrm{R}^2\mathrm{T}^2} - b\right)\frac{dp}{\mathrm{C}_p} \quad . \quad . \quad . \quad (124)$$

giving the Joule-Thomson effect. An *approximate* equation, ab neglected, gives, on integration:

$$\mathrm{C}_p(\mathrm{T}_2 - \mathrm{T}_1) = \left(\frac{2a}{\mathrm{RT}} - b\right)(p_2 - p_1).$$

The *inversion* in the Joule-Thomson effect (change of sign) occurs when:

$$2a/\mathrm{RT} - 3abp/\mathrm{R}^2\mathrm{T}^2 - b = 0$$

$$\text{or} \qquad \left(\mathrm{T} - \frac{a}{\mathrm{R}b}\right)^2 = \frac{a^2}{\mathrm{R}^2b^2} - \frac{3ap}{\mathrm{R}^2} \quad . \quad . \quad . \quad . \quad (125)$$

Approximately, $\mathrm{T} = 2a/\mathrm{R}b$.

If T is plotted against p from (125), with given values of a and b, a parabola is obtained, all points inside which represent cooling on

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[1] J. P. Dalton, *P. M.*, 1907, **13**, 525.

expansion, and all points outside it, heating. Instead of speaking of an *inversion point*, we should, therefore, speak of an *inversion curve*.[1] (Reduced inversion curve, § 47). For values of p greater than $a/3b^2$ there is always heating on expansion.

51. Berthelot's Equation.—In place of van der Waals' equation (97), D. Berthelot has proposed[2] one in which the constant a is replaced by a/T, *i.e.*, it now depends on the temperature:

$$(p + a/\mathrm{T}v^2)(v - b) = \mathrm{RT} \quad . \quad . \quad . \quad . \quad . \quad (126)$$

This gives exceedingly close agreement with experiment at pressures not exceeding a few atmospheres. When written in the form:

$$p = \mathrm{RT}/(v - b) - a/\mathrm{T}v^2$$

it gives, on differentiation:

$$\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v = \frac{\mathrm{R}}{v - b} + \frac{a}{v^2\mathrm{T}^2} \quad . \quad . \quad . \quad . \quad . \quad (127)$$

so that the pressure coefficient β now depends on the temperature, which is not the case with van der Waals' equation, but is found experimentally.

The values of a and b in terms of the critical constants are found by the method given in § 46, except that a is now replaced by a/T_c:

$$a = 3p_cv_c^2\mathrm{T}_c \text{ (128a)}; \; b = v_c/3 \text{ (128b)}; \; \mathrm{R} = 8p_cv_c/3\mathrm{T}_c \quad . \quad (128c)$$

Instead of these Berthelot uses the following *empirical* relations, which give the best results in practice:

$$a = \frac{16}{3}\,p_cv_c^2\mathrm{T}_c \text{ (129a)}; \; b = v_c/4 \text{ (129b)}; \; \mathrm{R} = \frac{32}{9}\frac{p_cv_c}{\mathrm{T}_c} \quad . \quad (129c)$$

On substituting (129) in (126) we find the *reduced Berthelot's equation*, as in § 47:

$$\left(\pi + \frac{16}{3}\frac{1}{\vartheta\phi^2}\right)\left(\phi - \frac{1}{4}\right) = \frac{32}{9}\vartheta \quad . \quad . \quad . \quad (130)$$

which holds for any mass of gas.

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[1] For thermal properties of CO_2 see Jenkins and Pye, *P. T.*, 1913, **213**, 67; 1915, **215**, 353; of NH_3, *Circular Bur. Stand.*, Washington, No. 142, 1923, (important in connection with refrigeration). Schulze, *A. P.*, 1916, **49**, 569, 585; Plank, *P. Z.*, 1914, **15**, 904.

[2] "Sur les thermomètres à gaz," *Mém. Bureau des poids et Mésures*, vol. 13, Paris, 1907; Nernst, "Theoret. Chem.," 8–10 Aufl., 1921, pp. 254 ff.; Jellinek, "Phys. Chem.," vol. 2, 1915, pp. 167 ff.; F. Henning, "Temperaturmessung," 1915, pp. 24 ff.

From (129) and (130), we find for 1 mol of gas :

$$\left(p + \frac{16}{3}\frac{p_c}{\vartheta\phi^2}\right)\left(v - \frac{v_c}{4}\right) = \mathrm{RT}$$

$\therefore \quad pv = \mathrm{RT}\left(1 + \frac{v_c}{4v} - \frac{16}{3}\frac{p_c}{p\vartheta\phi^2}\right)$ approximately, and, with the approximate substitution from (130) :

$$\pi\phi = \frac{32}{9}\vartheta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (130a)$$

in the correction terms only :

$$pv = \mathrm{RT}\left[1 + \frac{9}{128}\pi\tau(1 - 6\tau^2)\right] \quad . \quad . \quad . \quad (131)$$

where $\tau = 1/\vartheta = \mathrm{T}_c/\mathrm{T}$.

Equation (130) gives, on the substitution, $\pi = 1, \phi = 1, \vartheta = 1$, the equation $19/4 = 32/9$, which indicates that (130) cannot be true near the critical point.[1]

Equation (131) shows that at low temperatures, such that $6\tau^2 > 1$, gases are more compressible than the ideal gas. In the case of hydrogen T_c is very low, and even at fairly low temperatures $6\tau^2 < 1$; at higher temperatures nitrogen shows the same behaviour as hydrogen, *i.e.*, it is less compressible than the ideal gas. Equation (131) fits the observed *pv* curves at moderate pressures very well.

Let $1 + \frac{9}{128}\pi\tau(1 - 6\tau^2) = \lambda$, and let $p = p_1 = 1$ atm.

$\therefore \quad p_1v_1 = \lambda\mathrm{RT}$. If $pv \rightarrow p_0v_0$ as $p \rightarrow 0$ (§ 39), $p_0v_0 = \mathrm{RT}$

$\therefore$ *limiting density* = *normal density* × λ . . (131a)

For O_2, normal density 1·4290; $p_c = 50$ atm., $\mathrm{T}_c = 150°$ K.

$$\therefore \lambda = 1 - 0{\cdot}00074$$

$$\therefore \text{limiting density} = 1{\cdot}4290 \times (1 - 0{\cdot}00074) = 1{\cdot}4279$$

$\therefore$ *ideal molecular volume* = 32/1·4279 = 22·41 litres.

Multiply out (130) and neglect the small term $4/3.\vartheta\phi^2$:

$$\pi\phi - \frac{\pi}{4} + \frac{16}{3}\cdot\frac{1}{\phi\vartheta} = \frac{32}{9}\vartheta \quad . \quad . \quad . \quad . \quad (130b)$$

Differentiate with respect to ϑ (ϕ constant) :

$$\left(\phi - \frac{1}{4}\right)\frac{d\pi}{d\vartheta} = \frac{16}{3}\frac{1}{\phi\vartheta^2} + \frac{32}{9}.$$

---

[1] Cf. Porter, *P. M.*, 1922, **44**, 1020.

Substitute $(\phi - 1/4)$ from (130):

$$\frac{32\vartheta}{9}\frac{d\pi}{d\vartheta} = \left(\frac{16}{3}\cdot\frac{1}{\phi\vartheta^2}+\frac{32}{9}\right)\left(\pi+\frac{16}{3}\cdot\frac{1}{\vartheta\phi^2}\right)$$

$$= \frac{32\pi}{9}\left(1+\frac{3}{2}\frac{1}{\phi\vartheta^2}\right)\left(1+\frac{16}{3}\cdot\frac{1}{\pi\vartheta\phi^2}\right).$$

Substitute $1/\phi = 9\pi/32\vartheta$ from (130a) *in the correction terms*, and use the approximation $(1+a)(1+b) = 1+a+b$, where a and b are small compared with 1:[1]

$$\frac{\vartheta}{\pi}\cdot\frac{d\pi}{d\vartheta} = \left(1+\frac{27}{64}\frac{\pi}{\vartheta^3}\right)\left(1+\frac{27}{64}\frac{\pi}{\vartheta^3}\right)$$

$$= \left(1+\frac{27}{32}\frac{\pi}{\vartheta^3}\right) = \left(1+\frac{27}{32}\pi\tau^3\right).$$

Put $\pi = p/p_c$; $\vartheta = \mathrm{T}/\mathrm{T}_c$ on the left of the equation:

$$\therefore \qquad \beta = \frac{1}{p}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_v = \frac{1}{\mathrm{T}}\left(1+\frac{27}{32}\pi\tau^3\right). \quad . \quad . \quad . \quad (132)$$

This gives the correction for the constant volume gas thermometer. From Chappius' measured values of $\beta = 1/p_0 \,.\, (\partial p/\partial \mathrm{T})_v$, Berthelot calculated $\mathrm{T}_0 = 273{\cdot}09^0$ K as the absolute temperature of melting ice (cf. § 28).

From (131):

$$v = \frac{\mathrm{RT}}{p}\left[1+\frac{9}{128}\pi\tau(1-6\tau^2)\right] = \frac{\mathrm{R}}{p}\left[\mathrm{T}+\frac{9\pi\mathrm{T}_c}{128}\left(1-6\frac{\mathrm{T}_c^2}{\mathrm{T}^2}\right)\right]$$

Differentiate with respect to T (p constant):

$$\left(\frac{\partial v}{\partial \mathrm{T}}\right)_p = \frac{\mathrm{R}}{p}\left(1+\frac{108}{128}\pi\tau^3\right) \quad . \quad . \quad . \quad . \quad (133a)$$

Substitute for R/p from (131):

$$\frac{\mathrm{R}}{p} = \frac{v}{\mathrm{T}}\,\frac{1}{1+\frac{9}{128}\pi\tau-\frac{54}{128}\pi\tau^3} = \frac{v}{\mathrm{T}}\left(1-\frac{9}{128}\pi\tau+\frac{54}{128}\pi\tau^3\right)$$

$$\therefore \qquad \left(\frac{\partial v}{\partial \mathrm{T}}\right)_p = \frac{v}{\mathrm{T}}\left(1+\frac{108}{128}\pi\tau^3\right)\left(1-\frac{9}{128}\pi\tau+\frac{54}{128}\pi\tau^3\right)$$

$$\therefore \qquad \alpha = \frac{1}{v}\left(\frac{\partial v}{\partial \mathrm{T}}\right)_p = \frac{1}{\mathrm{T}}\left[1-\frac{9}{128}\pi\tau(1-18\tau^2)\right] \quad . \quad . \quad (133)$$

---

[1] *H. M.*, Appendix III.

The limiting values of a and β at zero pressure ($\pi = 0$) are both $1/T_0$ ($v_0 = p_0 = 1$).[1]

The *difference of molecular heats* is found [2] from (132) and (133a), neglecting terms of higher order:

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p = R\left(1 + \frac{27}{16}\pi\tau^3\right) \quad . \quad (134)$$

The equation (70) for the velocity of sound in a gas, together with (28) and (131) in the form:

$$\rho = \frac{1}{v} = \frac{M}{pRT}\left[1 - \frac{9}{128}\pi\tau(1 - 6\tau^2)\right] \quad . \ . \quad (135)$$

(v = *specific* volume = molecular volume divided by M) give [3]:

$$\gamma = \frac{C_p}{C_v} = u^2\left(\frac{\partial \rho}{\partial p}\right)_T = \frac{u^2 M}{RT}\left[1 - \frac{9}{64}\pi\tau(1 - 6\tau^2)\right] . \quad (136)$$

If $1 - \frac{9}{64}\pi\tau(1 - 6\tau^2) = \varphi$, and if λ_1, λ_2 are the wave-lengths of sound in two gases ($u = n\lambda$, where n = frequency), then:

$$\gamma_2/\gamma_1 = \frac{M_2}{M_1}\left(\frac{\lambda_2}{\lambda_1}\right)\frac{\varphi_2}{\varphi_1} \quad . \ . \ . \ . \ . \ . \quad (136a)$$

From (130) by differentiation, and the substitution $\pi\phi = \frac{32}{9}\vartheta$ in correction terms:

$$\left(\frac{d\pi\phi}{d\pi}\right)_\vartheta = \frac{1}{4}(1 - 6\tau^2) \quad . \ . \ . \ . \ . \ . \quad (137)$$

$$\left[\vartheta\left(\frac{d\pi}{d\vartheta}\right)_\phi - \pi\right] = \frac{32\tau}{3\phi^2} = \frac{27}{32}\pi^2\tau^3 \quad . \ . \ . \quad (138)$$

$$\left[\vartheta\left(\frac{d\phi}{d\vartheta}\right)_\pi - \phi\right] = \frac{9}{2}\tau^2 - \frac{1}{4} \quad . \ . \ . \ . \quad (139)$$

$$\left(\frac{d\phi}{d\pi}\right)_\vartheta = \frac{1}{\pi}\left(\frac{1}{4} - \phi - \frac{3}{2}\tau^2\right) \quad . \ . \ . \ . \quad (140)$$

For the *Joule effect*, we find from (95) and (133), with the approximate substitution: $dv = -RTdp/p^2$:

$$dT = \frac{RT_c}{C_v}\frac{dp}{p_c}\frac{27}{32}\tau^2 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (141)$$

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[1] Cf. Henning, "Temperaturmessung," pp. 65 ff. (reduction of gas scale to thermodynamic scale).

[2] Cf. Rücker, *A. P.*, 1921, **65**, 393; Schimank, *P. Z.*, 1916, **17**, 393.

[3] For applications of (134) and (136) see Partington, *P. R. S.*, 1921, **100**, 4; Partington and Cant, *P. M.*, 1922, **43**, 370; Partington and Shilling, *ibid.*, 1923, **45**, 416, and *F. S.*, 1923, **18**, 386.

For the Joule-Thomson effect, from (92) and (132) we find:

$$\left(\frac{dT}{dp}\right)_H = -\frac{9RT_c}{128p_cC_p}(1 - 18\tau^2) \quad . \quad . \quad . \quad . \quad (142)$$

For carbon dioxide at 0° C., with 1 atm. fall in pressure:

$$T_c = 304^\circ;\ R = 1{\cdot}984;\ p_c = 73 \text{ atm.};\ C_p = 8{\cdot}6$$

$$\therefore \Delta T = \frac{9 \times 1{\cdot}98 \times 304}{128 \times 73 \times 8{\cdot}6}\left[1 - 18\left(\frac{304}{273}\right)^2\right] \times 1$$

$$= -1{\cdot}31^\circ.$$

The observed fall in temperature under such conditions is 1·46°.

The calculation of the (theoretical) value of C_v when the gas is in the ideal state ($p = 0$, or $v \longrightarrow \infty$) may be made as follows. From (138):

$$\vartheta\frac{\partial^2\pi}{\partial\vartheta^2} \equiv \frac{\partial}{\partial\vartheta}\left(\vartheta\frac{\partial\pi}{\partial\vartheta} - \pi\right) = -\frac{32}{3\vartheta^2\phi^2}$$

From (51): $(\partial C_v/\partial v)_T = T\,.\,\partial^2p/\partial T^2 = p_c\vartheta/T_c\,.\,\partial^2\pi/\partial\vartheta^2$

$$= -32p_c/3\vartheta^2\phi^2T_c = -32p_cv_c^2/3\vartheta^2v^2T_c$$

$$\therefore \qquad C_v = f(v) + \frac{p_cv_c^2}{T_c\vartheta^2}\cdot\frac{32}{3v}.$$

When $v \longrightarrow \infty$, or $p \longrightarrow 0$, let $C_v \longrightarrow C_v^0$:

$$\therefore \qquad C_v = C_v^0 + \frac{32}{3}\frac{p_cv_c^2}{T_c}\cdot\frac{1}{\vartheta^2v}$$

But (129) $p_cv_c/T_c = 9R/32$, and (130) $\pi\phi = 32\vartheta/9$, $\vartheta = 1/\tau$

$$\therefore \qquad C_v = C_v^0 + \frac{27}{32}R\pi\tau^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad (143)$$

C_v^0 should be used in considerations as to the partition of kinetic energy in gas molecules, as it contains no contributions due to potential energy.[1]

The temperature change on *adiabatic change of volume* is equal to the temperature change due to external work (ideal gas) plus that due to internal work (Joule effect):

$$dT = -pdv/C_v + dT'.$$

But $dv = -RTdp'/p^2$ where dp' = pressure change to produce the change of volume dv isothermally; p = initial pressure ∴ from (141):

$$dT = \frac{RT}{C_v}\frac{dp'}{p}\left(1 + \frac{27}{32}\pi\tau^3\right)$$

$$\therefore C_v = R\frac{d\ln p'}{d\ln T}\left(1 + \frac{27}{32}\pi\tau^3\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (144)$$

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[1] Cf. Partington, *F. S.*, 1922, **17**, 734; Bartels and Eucken, *Z. p. C.*, 1921, **98**, 70; Millar, *J. A. C. S.*, 1923, **45**, 874.

Let dp_v = increase of pressure due to increase of temperature $d\mathrm{T}$ at constant volume, then, from (132):

$$d\ln \mathrm{T} = d\ln p_v\left(1 - \frac{27}{32}\pi\tau^3\right)$$

$$\therefore\ \mathrm{C}_v = \mathrm{R}\frac{d\ln p'}{d\ln p_v}\left(1 + 2\cdot\frac{27}{32}\pi\tau^3\right)$$

$$= \frac{d\ln p'}{d\ln p_v}(\mathrm{C}_p - \mathrm{C}v) \text{ from (134)}$$

$$\therefore\ \gamma - 1 = d\ln p_v/d\ln p' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (145)$$

The adiabatic pressure change for a given change of volume is equal to the pressure change due to the change of volume at constant temperature (dp') plus the pressure change due to the change of temperature at constant volume $\therefore$ $dp_{\mathrm{Q}} = dp' + dp_v$; hence, if p is the initial pressure: $dp_{\mathrm{Q}}/p = dp'/p + dp_v/p$ or $d\ln p_{\mathrm{Q}} = d\ln p' + d\ln p_v$

$$\therefore\ \gamma = \frac{d\ln p_{\mathrm{Q}}}{d\ln p'} = \frac{\log p_1 - \log \mathrm{P}}{\log p_1 - \log p_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (146)$$

with the same notation as in (65). The equation used by Röntgen, therefore, requires no correction when the pressure differences are small.

To obtain the correction for Lummer and Pringsheim's equation [66], we must replace p_2 in (146) by **P** and the temperatures, T_1 corresponding with p_1 and T_2 corresponding with **P**, the pressure after adiabatic expansion. If the volume remained constant after expansion and the temperature changed to T_1 the pressure would be p_2, Now

$$d\ln p_v\, d\ln \mathrm{T} = 1 + 27/32\ .\ \pi\tau^3$$

$$\therefore\ \ln\frac{p_2}{\mathrm{P}} = \int_{\mathrm{T}_2}^{\mathrm{T}_1}(1 + \frac{27}{32}\pi\tau^3)d\ln \mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad (147)$$

The integration cannot be effected exactly, but if we put:

$$\pi = (p_1 + \mathrm{P})/2p_c \text{ and } 1/\tau = (\mathrm{T}_1 + \mathrm{T}_2)/2\mathrm{T}_c$$

$$\ln\frac{p_2}{\mathrm{P}} = (1 + \frac{27}{32}\pi\tau^3)\ln\frac{\mathrm{T}_1}{\mathrm{T}_2}.$$

Substitute $\ln p_2$ in (146)

$$\therefore\ \gamma = \ln(p_1/\mathrm{P})/[\ln(p_1/\mathrm{P}) - (1 + 27/32\ .\ \pi\tau^3)\ln(\mathrm{T}_1/\mathrm{T}_2)] \quad . \quad (148)$$

$\therefore$ by comparison with [66] and rearrangement:

$$\gamma = \gamma'\left[1 + (\gamma' - 1)\frac{27}{32}\pi\tau^3\right] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (149)$$

where γ' is the value calculated by [66], *i.e.*, on the assumption that the gas is ideal.

There is little doubt that Berthelot's equation gives most accurate results with gases under moderate pressures, say up to 5 atm. At high pressures it becomes much less accurate, and other equations may then be used, but with less certainty. Among these equations may be mentioned those of:

1. Clausius[1]:

$$\left(p + \frac{a}{\mathrm{T}(v - \beta)^2}\right)(v - b) = \mathrm{RT};$$

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[1] Clausius, *A. P.*, 1880, **9**, 337. At *low* temperatures, see Sackur, *Ber.*, 1914, **47**, 1318; Shaha and Basu, *P. M.*, 1918, **36**, 199; cf. Jeans, *C. S.* 1923, **123**, 3398.

2. Dieterici[1] (two equations):

$$(p + a/v^{5/3})(v - b) = \mathrm{RT};$$

$$pe^{a/\mathrm{RT}v}(v - b) = \mathrm{RT}.$$

3. Wohl[2]:

$$\left(p + \frac{a}{\mathrm{T}v(v - b)} - \frac{c}{\mathrm{T}^2v^3}\right)(v - b) = \mathrm{RT}.$$

The latter gives good results at high pressures[3]; it reduces to Berthelot's equation at small pressures. As to the applicability of any characteristic equation at high temperatures nothing definite can yet be asserted, since there are no adequate experimental results. There is no reason to suppose, however, that an equation which applies at lower temperatures under a given pressure will deviate *largely* from accuracy at higher temperatures under the same pressure. (On a modified Berthelot equation, see A. W. Porter.[4])

4. Callendar[5] puts (for moderate ranges of pressure): $\mathrm{V} - b = \mathrm{RT}/p - c$. The small term c is the "coaggregation volume" (*i.e.*, the diminution in volume produced by coaggregation or pairing of molecules); it may be written $c = c_1 (\mathrm{T}_1/\mathrm{T})^n$, where c_1 is the value of c at some standard temperature T_1 (preferably 373°·1 K.) and n is a constant which for steam = 10/3. Callendar proposes the equation $p/\mathrm{RT} = 1/v - c'/v^2 + c'c''/v^3$, for the liquid and gaseous state, c' and c'' being any arbitrary functions of temperature. At the critical point, from (99), we see that $p_c/\mathrm{RT}_c = 3v_c = 3c'_c = 9c''_c$. c' is of the form $(c - b)$ and c'' is $5b/3$, so that $v_c = 5b$.

EXAMPLES VIII.

1. The values of a and b referred to 1 mol of methylamine with the mm. Hg as unit of pressure and 1 litre as unit volume are $a = 5620$ and $b = 0{\cdot}061$. Find the values referred to the c.c. as unit volume and 1 atm. as unit pressure. Find the value of R in van der Waals' equation in the two cases.

2. The critical temperature of ammonia is 130° C., and the critical pressure 115 atm.; find the values of a and b in van der Waals' equation, naming the units, and plot the isotherms for 17° C., 130° C., and 160° C.

3. The values of a and b for nitrogen are: $a = 1660$, $b = 1{\cdot}32$ (referred to 1 gm., 1 c.c. and 1 atm.). Find θ_c, p_c and v_c.

4. T_c for ether is 193·8° C. and $p_c = 2706$ cm.Hg. Calculate the constants a and b (van der Waals') for ether and thence find the critical density.

5. Plot a series of isotherms for CO_2, using the equation:[6]

$$\left(p + \frac{0{\cdot}00874}{v^2}\right)(v - 0{\cdot}0023) = 1{\cdot}00646\,\mathrm{T}$$

6. Show that the mean compressibilities of two fluids between equal reduced pressures at the same reduced temperature are inversely proportional to their critical pressures.

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[1] Dieterici, *A. P.*, 1899, **69**, 685; 1901, **5**, 51; 1903, **12**, 144, 154. Modified van der Waals' equation: von Jüptner, *Z. p. C.*, 1908, **63**, 579; 1910, **73**, 343.

[2] *Z. p. C.*, 1914, **87**, 1; *ibid.*, 1921, **99**, 207, 226, 234; cf. Carl, *ibid.*, 1922, **101**, 238.

[3] Nernst, "Theoret. Chem.," 8–10 Aufl., p. 257.

[4] *P. M.*, 1922, **44**, 1020.

[5] "Properties of Steam," London, 1920, p. 184.

[6] Cf. Nernst, "Theoret. Chem.," 8 Aufl., p. 230.

7. Show that the mean coefficients of expansion of two fluids between equal reduced temperatures at the same reduced pressure are inversely proportional to their critical temperatures.

8. Find the values of a and b in van der Waals' equation for the following substances, taking the gm., atm., and litre as units :

	H_2.	N_2.	CO_2.	NH_3.	SO_2.
p_c atm. . .	20	33	73	115	78·9
θ_c °C.	−234·5	−146	31·1	130	155·4

9. Show from Berthelot's equation that a gas obeys Boyle's law at a temperature 2·44 T_C. Calculate this for H_2, N_2, CO_2, NH_3. Given: H_2, $a = 0·19 \times 10^6$, $b = 23$; N_2, $a = 1·31 \times 10^6$, $b = 37·3$; CO_2, $a = 3·61 \times 10^6$, $b = 42·8$; NH_3, $a = 4·05 \times 10^6$, $b = 36·4$. (Units, gm., c.cm., atm.)

10. Show from Berthelot's equation that $M = [(\rho RT)/p]\,(1 + Ap)$, where ρ = density of gas, M = mol. wt., and A is a constant at a temperature T, $A = 9T_C(T^2 - 6T_C^2)/128p_CT^2$.

11. The values of pV/RT per mol of SO_2 at 0° C. are 0·9973 when $p = 0·1$ atm. and 0·9759 when $p = 1$ atm. The density of SO_2 at S.T.P. (0° C., 1 atm.) is 2·9266 gm./lit. Find the atomic weight of sulphur (O = 16). (See §§ 39, 51.)

12. The specific volume of saturated $SnCl_4$ vapour is 78·4 at 130° C. and 22·0 at 190° C. (Thorpe and Pierre), whilst the specific volume of liquid $SnCl_4$ is 0·5166 and 0·5696 at the same temperatures respectively (Young). If the critical density of $SnCl_4$ is 0·7423 gms. per c.c., find the critical temperature and pressure and thence deduce the values of a and b in van der Waals' equation for this substance.

13. Plot the rectilinear diameter of Cailletet and Mathias for ether from the following figures due to Centnerszwer (1907), d being the density of liquid or vapour at the temperature t° C. :

d.	*t.*	*d.*	*t.*	*d.*	*t.*
0·0952 ...	172·6	0·2231 ...	194·05	0·3593 ...	190·8
0·1167 ...	182·15	0·2558 ...	194·5	0·3734 ...	188·9
0·1389 ...	187·15	0·2843 ...	194·1	0·3844 ...	187·3
0·1822 ...	192·3	0·3094 ...	193·5	0·4456 ...	175·7
				0·4608 ...	169·3

Thence show that the critical temperature is 194·4° C. (which agrees with Young's observed value).

14. In the case of normal pentane at 0° C. the densities of liquid and vapour are 0·6454 and 0·0008. At 190° C. the values are 0·3445 and 0·1269. The critical temperature is 197·2° C. Find the critical density. (Young gives 0·2323.)

15. According to Sajontchewski, the vapour pressure of SO_2 is 60 atm. when T = 412·9° ; that of ether is 28·4 atm. when T = 445·8°. The critical constants are : SO_2 : $T_C = 428·4°$; $p_C = 78·9$ atm. ; $(C_2H_5)_2O$: $T_C = 463°$; $p_C = 36·9$ atm. Test the equation $\pi_V = f(\vartheta)$.

16. The van der Waals' constants for aniline are $b = 137$ and $a = 26·6 \times 10^6$, the pressure being expressed in atmospheres and the volume in c.cms. Plot the inversion curve for aniline.

17. Plot the inversion curve for ammonia, given $a = 4·05$ and $b = 36·4 \times 10^{-3}$, the volume being expressed in litres and the pressure in atmospheres.

18. The critical data for CO_2 are as follows : $T_C = 304°$ K and p_C = 73 atm. (Cardoso), $a = 3·61 \times 10^6$, $b = 42·8$ (atm. unit of pressure ; c.cm. unit

of vol.). Amagat found the following relations between p and v for this gas:

	$\theta=40°$ C.		$\theta=80°$ C.
1 vol.	$p =$ 1·148 atm.	1 vol.	$p =$ 1·295 atm.
0·024 vol.	$p =$ 39·0 „	0·024 vol.	$p =$ 46·6 „
0·013 „	$p =$ 59·7 „	0·0164 „	$p =$ 63·5 „
0·010 „	$p =$ 68·6 „	0·010 „	$p =$ 91·3 „
0·0058 „	$p =$ 83·1 „	0·0058 „	$p =$ 128·8 „
0·0032 „	$p =$ 98·0 „	0·0025 „	$p =$ 346·0 „
0·002 „	$p =$ 470·0 „		

Test van der Waals' reduced equation of state with these figures.

19. The boiling points of CCl_4, normal pentane, and acetic acid are 76·7°, 36·2°, and 118·5°. The latent heats are given by Young as follows:

	80°.	140°.	200°.
CCl_4	46·00	39·92	32·61 gm. cal.
n-pentane	75·33	56·58	24·68 (190°) gm. cal.
Acetic acid	91·59	91·83	85·55 „

Find the values of Trouton's constant for the three substances.

20. The van der Waals' constants for H_2 are $a = 0·19 \times 10^6$, $b = 23$, taking the c.cm. as the unit of volume and the atmosphere as the unit of pressure. Show that below − 73° C. hydrogen becomes cooler on expansion.

21. Calculate the inversion point of CO_2, given the van der Waals' constants are $a = 3·61 \times 10^6$ and $b = 42·8$, the c.c. being the unit of volume and the atmosphere the unit of pressure.

CHAPTER IX

Dilute Solutions

52. Solutions of Gases in Liquids.—The amount of gas dissolved by a liquid in equilibrium: free gas $\rightleftarrows$ dissolved gas, depends on (i.) the chemical characters of the gas and liquid, (ii.) pressure, and (iii.) temperature.

The effect of pressure is given by **Henry's Law**[1]: *The amount of gas dissolved at a given temperature is proportional to the pressure.* Dalton found in 1803[2] that, with a *mixture of gases*, the amount of each dissolved is independent of the presence of the other gases, and is *proportional to the partial pressure* (§§ 80, 84) of the gas in the mixture in equilibrium with the liquid.

The gas pressure is proportional to the *concentration* $c = n/V =$ *number of mols per litre*, $\therefore$ (57a) may be written:

$$p = cRT \quad . \quad . \quad . \quad . \quad . \quad . \quad [150]$$

$\therefore$ from Henry's law: (*concentration in solution*) $\div$ (*concentration in gas space*) $=$ *constant.* This ratio (at a given temperature) is defined by Ostwald as the *solubility*, *s*, of the gas in the liquid.

Let a mol of gas, occupying a volume v_0 at a pressure p_0, be brought in contact with a volume V of liquid in a cylinder under a piston. It is required to find the pressure, p, when the volume of gas has been reduced to x in contact with the liquid, assuming the volume of liquid to remain constant. We have: $p_0v_0 = RT$, and $px = nRT$, where n mols of gas remain undissolved, and $1 - n$ mols dissolve.

$$s = \frac{\text{concentration in liquid}}{\text{concentration in gas}} = \frac{(1-n)}{V}\Big/\frac{n}{x} = \frac{(1-n)x}{nV} = \frac{p_0v_0 - px}{pV}$$

$$\therefore p = p_0v_0/(x + sV) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [151]$$

If $x = 0$, $V = p_0v_0/ps =$ least volume of liquid required to dissolve 1 mol of gas under pressure p. Also $s = p_0v_0/pV =$ *conc. in liq./conc. in gas.*[3]

53. Osmotic Pressure.—Certain septa exhibit selective permeability towards dissolved substances.[4] Thus, copper ferrocyanide deposited in the walls of a porous pot will allow solvent, *e.g.*, water to pass through, but not dissolved sugar, or other substances. If a liquid solution, say of sugar in water, is separated from the pure solvent by such a *selectively permeable septum*, and if π, π' are the pressures which must be applied to the solvent and solution, respectively, to maintain equilibrium (Fig. 21), then:

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[1] *P. T.*, 1803, 93, 29; Ostwald, "Lehrbuch," I., 612 ff.

[2] *M. M.*, 1805, [ii.], 1, 271.

[3] Cf. Sander, *Z. p. C.*, 1912, 78, 513.

[4] M. Traube, 1867; "Ges. Abh.," 1899, pp. 213 ff.

$$\pi' - \pi = P_{\pi, T} \quad (152)$$

is defined as the *osmotic pressure of the solution* at the given temperature and with the solvent under the pressure π.[1] It is independent of the nature of the septum provided its selective permeability is perfect.

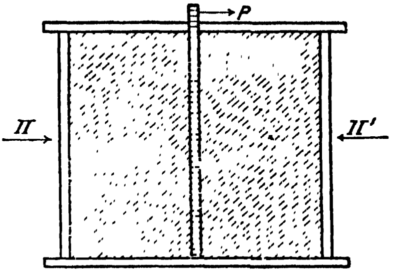

FIG. 21.

Consider two septa [a] and [β], and let the osmotic pressures of identical solutions separated from pure solvent by [a] and [β] be P_a and P_β. Then if the septum is moved so as to separate a volume δV of solvent from a large volume of solution through [a], the work spent is $P_a \delta V$. If the separated solvent is readmitted to the solution through the septum [β], the work done is $P_\beta \delta V$. An isothermal cycle has been completed, hence, by (44), $P_a \delta V - P_\beta \delta V = 0$, or $P_a = P_\beta$.

The laws of osmotic pressure were first investigated from the point of view of thermodynamics by van't Hoff.[2] The discussion below is due to Lord Rayleigh [3]; the complete theory, for all concentrations of solution, has been worked out by A. W. Porter.[4]

Consider 1 mol of gas and a volume V of solvent just sufficient to dissolve all the gas at a pressure p_0. Let the volume of gas at p_0 be v_0. Then $s = v_0/V$. The gas can be dissolved reversibly in the solvent by first expanding reversibly to a very large volume, then bringing in contact with the solvent under gradually increasing pressure, so that at each stage the pressure of the gas is equal to that (given by Henry's law) corresponding with the amount dissolved. The last trace of gas goes into solution under pressure p_0.

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[1] Experimental details, see Findlay, "Osmotic Pressure," London, 1919.

[2] *Z. p. C.*, 1887, **1**, 481; *P. M.*, 1888, **26**, 81.

[3] *Nature*, 1897, **55**, 253.

[4] *P. R. S.*, 1907, **79**, 519; 1908, **80**, 457, to which memoirs the reader is referred for details; cf. Vegard, *P. M.*, 1907, **18**, 606, and Magie, *P. R.*, 1912, **35**, 272; *ibid.*, 1917, **10**, 64.

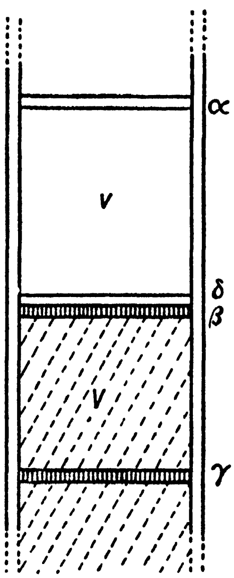

Fig. 22.

Let the gas and liquid be contained in a cylinder fitted with an impervious piston a, a fixed diaphragm β permeable to gas but not to liquid, a piston γ permeable to liquid but not to dissolved gas, and an impervious shutter δ which can be placed over β as desired (Fig. 22), and let the following isothermal and reversible process be carried out:

(1) Expand the gas to the very large volume x, keeping δ over β. The pressure p at any stage of the expansion is $p = p_0v_0/x$, $\therefore$ work gained in expansion:

$$= \int_{v_0}^{x} pdv = p_0v_0 \int_{v_0}^{x} dx/x = p_0v_0 \, . \ln (x/v_0).$$

(2) Remove δ and dissolve the gas reversibly by pressing down a. (No change in the volume of liquid occurs when gas dissolves, $\therefore$ β and γ may be kept in position.) The pressure at any stage is given by [151] $\therefore$ work gained:

$$= - \int_{0}^{x} pdv = - p_0v_0 \int_{0}^{x} dx/(x + s\mathrm{V}) = - p_0v_0 \, . \ln (x + s\mathrm{V})/s\mathrm{V}$$ [1]

$\therefore$ total work *spent* in getting the gas into solution:

$$= p_0v_0 \left\{ \ln \frac{x + s\mathrm{V}}{s\mathrm{V}} + \ln \frac{v_0}{x} \right\} = p_0v_0 \left\{ \ln \frac{x + s\mathrm{V}}{x} + \ln \frac{v_0}{s\mathrm{V}} \right\} \rightarrow 0$$

since $v_0 = s\mathrm{V}$, and $(x + s\mathrm{V})/x \rightarrow 1$ as $x \rightarrow \infty$. The gas has dissolved reversibly without expenditure of work.

(3) Raise a and γ simultaneously through the spaces v_0 and V, respectively, so that the solution maintains a constant composition throughout, and p_0 and P are constant. The work gained is $p_0v_0 - \mathrm{PV}$.

The cycle is now complete, hence by (44):

$$\mathrm{PV} = p_0v_0 = \mathrm{RT} \quad . \ . \ . \ . \ . \ . \quad [153]$$

For n mols of gas $p_0v_0 = n\mathrm{RT}$, $\therefore$ $\mathrm{PV} = n\mathrm{RT}$, or:

$$\mathrm{P} = \mathrm{RT} \,.\, n/\mathrm{V} = c\mathrm{RT} \quad . \quad . \quad . \quad [153\mathrm{a}]$$

Equation [153], true for all temperatures, shows that the laws of osmotic pressure for dilute solutions are *formally* identical with the laws of ideal gases. *At a given temperature osmotic pressure is proportional to concentration, or inversely proportional to volume* (Boyle's Law); *at a fixed volume osmotic pressure is proportional to absolute temperature* (Gay Lussac and Charles's Law); and, since the constant R is the same in both cases, *equimolar amounts of different solutes in equal volumes of any solvent exert equal osmotic pressures* (Avogadro's Law). It is assumed that the molecular weights of the solute in the various solvents are equal, which is not always the case in practice. Since we may assume all substances to have some volatility, the proof is general.

The experiments of Perrin and others lead us to suppose the same *cause* for the pressure in the case of gases and solutions, *i.e.*, molecular bombardment.[1] This question lies outside Thermodynamics, which enables us to deduce the laws of osmotic pressure without knowing anything of the mechanism of the process, but at the same time tells nothing about this mechanism.

Direct measurements of the osmotic pressures of aqueous solutions, first made by Pfeffer,[2] later by Lord Berkeley and E. G. J. Hartley, and by Morse,[3] show that for small concentrations ($c < 0{\cdot}1$) the agreement with [153a] is good, but as c increases the observed osmotic pressure becomes increasingly higher than the calculated value. A. W. Porter[4] shows that the ideal gas formula may then be replaced as a second approximation by Hirn's formula (§ 45): $\mathrm{P}(v - b) = \mathrm{RT}$, and interprets this in terms of hydration of the solute.

54. Vapour Pressure of Dilute Solutions.—Let a solution contain w gms. of non-volatile solute in W gms. of volatile solvent. Let m and M be the molecular weights of the solute and solvent, respectively. The numbers of mols present are $n = w/m$ and $\mathrm{N} = \mathrm{W}/\mathrm{M}$. Let there be given also an additional mass W′ of pure solvent, *i.e.*, $\mathrm{N}' = \mathrm{W}'/\mathrm{M}$ mols, where N′ is small compared with N. Let the vapour pressures of the pure solvent and of the solution be p_0 and p, respectively.

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[1] See Perrin, "Brownian Movement and Molecular Reality," trans. F. Soddy, 1910; *ibid.*, "Les Atomes," 5th edit., 1914 (Eng. tr. "Atoms," 2nd edit., 1923); Svedberg, "Die Existenz der Moleküle," 1912; *F. S.*, 1917, **13**, 119 ff.

[2] "Osmotische Untersuchungen," Leipzig, 1877.

[3] For references to osmotic pressure measurements, see Jellinek, "Phys. Chem.," II., 706 ff., and Findlay's "Osmotic Pressure," London, 1919; cf. also Wegscheider, *Z. p. C.*, 1920, **94**, 739; Larmor, "Æther and Matter," p. 287.

[4] *F. S.*, 1917, **13**, 123.

The N′ mols of solvent are now added to the solution isothermally and reversibly as follows:

(1) Evaporate the N′ mols of solvent isothermally and reversibly under the vapour pressure p_0. Let $v' =$ volume of liquid, $V_0' =$ volume of vapour, then the work done is:

$A_1 = p_0(V_0' - v') = p_0V_0'$ approximately $= N'RT$ if the vapour obeys the gas laws.

(2) Expand the N′ mols of vapour isothermally and reversibly from the pressure p_0 of the pure solvent to the pressure p of the solution at the same temperature T. The work done is:

$$A_2 = N'RT \,.\, \ln (V'/V_0') = N'RT \,.\, \ln (p_0/p)$$

where V_0' and V' are the volumes of the vapour under the pressures p_0 and p, respectively.

(3) Bring the vapour in contact with the solution, with which it is now in equilibrium, and condense it under the pressure p, which, since N′ is small compared with N, will remain sensibly constant throughout the process. The work done is:

$$A_3 = -p(V' - \Delta v) = -pV' \text{ approximately} = -N'RT,$$

where Δv is the increase in volume of the solution, which is negligible in comparison with the volume of the vapour.

The process is complete and the total work done is:

$$A_1 + A_2 + A_3 = N'RT + N'RT \,.\, \ln (p_0/p) - N'RT$$
$$= N'RT \,.\, \ln (p_0/p).$$

If $N' = 1$, the work done per mol of solvent transferred to the solution is:

$$\mathbf{A = RT \,.\, \ln (p_0/p)} \quad . \quad . \quad . \quad . \quad [154]$$

Since the solution and solvent would mix spontaneously, this work is positive, by the principle of dissipation of energy (§ 60), hence $p_0 > p$, *i.e.*, the vapour pressure of the solution is lower than that of the pure solvent at the same temperature.

The N′ mols of solvent may be separated again isothermally and reversibly by making use of a selectively permeable septum. Let the solution be enclosed in a cylinder fitted with a piston permeable only to pure solvent, and let the pressure be raised to the osmotic pressure of the solution, P. Since the solution is nearly incompressible, this may be done without sensible expenditure of work. Now let the septum be brought in contact with solvent, with which the solution is in equilibrium under the pressure P, and let N′ mols of solvent be squeezed out. The pressure remains sensibly equal to P during the process, since N′ is small compared with N. The work done is $-P\Delta v$.

The system is now in the initial state, ∴ by (44), total work = 0 :

$$\therefore \qquad P\Delta v = N'RT \,.\, \ln (p_0/p) \quad . \quad . \quad . \quad . \quad . \qquad [155]$$

But Δv = volume of N′ mols of solvent (assuming total volume of solution after adding the N′ mols of solvent = volume of original solution, *plus* volume of solvent added). Let n' = no. of mols of solute in a volume Δv of solution. Then, by [153a]: $P\Delta v = n'RT = N'RT \,.\, \ln (p_0/p)$,

$$\therefore \qquad \ln \frac{p_0}{p} = \frac{n'}{N'} = \frac{\text{no. of mols of solute}}{\text{no. of mols of solvent}}. \quad . \quad . \quad . \qquad [155a]$$

But $\ln \frac{p_0}{p} = \ln \left(1 + \frac{p_0 - p}{p}\right) = \frac{p_0 - p}{p}$ when $p_0 - p$ is small, *i.e.*, when the solution is dilute.[1] Hence :

$$(p_0 - p)/p = n'/N', \text{ or (dropping the accents) :}$$

$$\boldsymbol{(p_0 - p)/p_0 = n/(N + n)} \quad . \quad . \quad . \qquad \mathbf{[156]}$$

This law was discovered experimentally by Raoult in 1886.[2] The relation between p_0 and p was deduced from thermodynamics independently by Gouy and Chaperon [3] in 1888, and by Arrhenius [4] in 1889.

N′ refers to the number of mols of vapour transferred, *i.e.*, the molecular weight of the vapour of the solvent is involved. The method gives no indication of the molecular weight of the *liquid* solvent.

In a very dilute solution n may be neglected in comparison with N

$$\therefore \qquad \boldsymbol{(p_0 - p)/p_0 = n/N} \quad . \quad . \quad . \quad . \qquad \mathbf{[156a]}$$

55. Boiling Points of Dilute Solutions.—Let AA′, BB′ in Fig. 23 represent portions of the vapour pressure curves of solvent and solution, respectively. Then [156] shows that the relative lowering of vapour pressure $(p_0 - p)/p_0$ is independent of temperature (Law of von Babo) (cf. § 95). Draw PQ, QR parallel to the axes, then : PQ = RQ tan PRQ

---

[1] Cf. *H. M.*, § 36.

[2] *C. R.*, 1886, **103**, 1125, and later papers. Cf. his book, "Tonométrie," Paris, 1900. For measurements of vapour pressures, cf. Jellinek, "Phys. Chem.," Vol. II., pp. 752 ff. Vapour pressures of liquids in contact with gases: F. H. Campbell, *F. S.*, 1915, **10**, 197. Vapour pressure of conc. solutions: D. O. Wood, *ibid.*, 1915, **11**, 28; of solutions: Hartung, *ibid.*, 1920, **15**, 150. Lovelace, Frazer and Sease, *J. A. C. S.*, 1921, **43**, 102; abnormality of KCl about 0·6 molar. Lotz and Frazer, *J. A. C. S.*, 1921, **43**, 2501.

[3] *A. C. P.*, 1888, **13**, 124.

[4] *Z. p. C.*, 1889, **3**, 115.

$$\therefore \quad p_0 - p = \delta T \tan PRQ$$

where δT is the elevation of boiling point of the solvent if p, corresponding with the ordinate of RQ, is the pressure on the surface of the liquid.

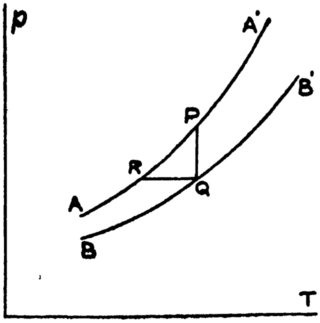

FIG. 23.

If RQ is small, then (*H. M.*, § 69) :

tan PRQ = dp/dT for the pure solvent $= p_0\lambda_e/RT_0^2$ from [82], where T_0 is the boiling point of the pure solvent,

$$\therefore \qquad (p_0 - p)/p_0 = \lambda_e \delta T/RT_0^2 \quad . \quad . \quad . \quad . \quad [157]$$

thence, from [156] :

$$n/(N + n) = \lambda_e \delta T/RT_0^2 = \lambda_e \delta T/2T_0^2 \quad . \quad . \quad [158]$$

where λ_e and R are in cals., R = 1·987 = 2, approximately. Thence, for 1 mol of solute in 100 mols of solvent :

$$\mathbf{E = \delta T = 0{\cdot}02T_0^2/\lambda_e} \quad . \quad . \quad . \quad . \quad \mathbf{[159]}$$

giving the *molecular elevation of boiling point*, E, in terms of properties of the pure solvent. This equation, deduced by van't Hoff in 1887, was verified by Beckmann in 1889.[1] It forms the basis of a method for the determination of molecular weights.

If $p_0 - p$ is too large to justify the assumption of [157], equation [82] may be integrated on the assumption that λ_e is constant :

$$\ln p = -\lambda_e/RT + \text{const.}$$

where p is the vapour pressure of the *pure solvent* at the boiling point T of the solution. At the boiling point T_0 of the pure solvent (p_0 = 1 atm.) :

$$\ln p_0 = -\lambda_e/RT_0 + \text{const.}$$

$$\therefore \quad \ln\frac{p_0}{p} = \frac{n}{N}\,(\text{approx.}) = \frac{\lambda_e}{R}\left[\frac{1}{T_0} - \frac{1}{T}\right] = \frac{\lambda_e}{RTT_0}\,\delta T \quad . \quad [160]$$

If we put $TT_0 = T_0^2$, approximately, this gives [159].[2]

---

[1] Cf. Beckmann and Liesche, *Z. p. C.*, 1914, **86**, 337.

[2] Molecular weights from boiling points : cf. Jellinek, II., 786 ff. ; theory : Beckmann and Liesche, *Z. p. C.*, 1914, **86**, 337 ; 1914, **88**, 419 ; **89**, 111.

56. Calculation of Osmotic Pressure.—In equation [155] put $N' = N$, then if M and ρ are the molecular weight and density of the solvent,

$$\Delta v = NM/\rho$$

$$\therefore \qquad P = (\rho/M) \, . \, RT \, . \ln (p_0/p) \quad . \; . \; . \; . \quad [161]$$

To express P in atm. take 1 litre as unit volume and put $R = 0{\cdot}082$ litre atm./degree. Thus:

$$P = \frac{0{\cdot}082 \times 1000\rho}{M} \ln \frac{p_0}{p} \quad . \; . \; . \; . \quad [162]$$

From [160] and [161] when $\lambda_e/M = L_e$, and $T - T_0 = \delta T$:

$$P/\rho L_e = \delta T/T_0 \quad . \; . \; . \; . \; . \; . \; . \quad [163]$$

To express P in atm. put L_e cal. $= L_e/24{\cdot}2$ litre atm., and use [162]:

$$P = \delta T \, . \, 1000\rho L_e/24{\cdot}2 \; T_0 \text{ atm.} \quad . \; . \; . \quad [164]$$

57. Freezing Points of Dilute Solutions.—The freezing point of a solution is the temperature at which solution is in equilibrium with frozen solvent (" ice "). It is assumed that pure solvent only separates on freezing, which is usually the case. The vapour pressure of the solution at the freezing point must therefore be equal to the vapour pressure of solid solvent at the same temperature (Guldberg, 1870).[1]

The vapour pressure curves of solution and ice must intersect at the freezing point. But the vapour pressure curve of the solution lies below that of the pure solvent throughout its length, and since the latter cuts the vapour pressure curve of ice at the freezing point of the pure solvent, the vapour pressure curve of the solution must cut the vapour pressure curve of ice at a temperature below the freezing point of the pure solvent. Thus, *the freezing point of the solvent is lowered by addition of solute.*

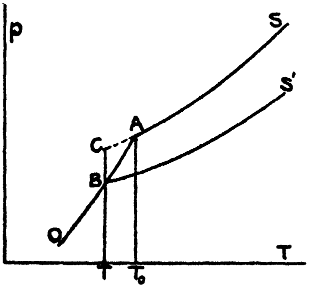

FIG. 24.

In Fig. 24 OA, AS represent the vapour pressure curves of ice and liquid solvent respectively, BS′ that of the dilute solution.

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[1] *C. R.*, 1870, **70**, 1349; Ostwald's *Klassiker*, No. 139 (1903), p. 54: some of Guldberg's memoirs in this collection are of great interest.

AC is the vapour pressure curve of the supercooled liquid. T_0 is the freezing point of pure solvent, T that of the solution.

Along CS we have $d \ln p_e/dT = \lambda_e/RT^2$, and along OA, $d \ln p_s/dT = \lambda_s/RT^2$, where p_e and p_s are the vapour pressures of liquid and solid, and λ_e and λ_s the *molecular* heats of evaporation and sublimation, respectively. It is assumed that the vapour obeys the gas laws, which will be very approximately true, since the pressures are small. On the assumption that λ_e and λ_s are constant:

$$\ln p_e = -\lambda_e/RT + c', \text{ and } \ln p_s = -\lambda_s/RT + c'',$$

where c' and c'' are constants. At T_0 we have $p_e = p_s = p_0'$, where p_0' is the common vapour pressure of ice and liquid solvent at T_0.

$$\text{Thus: } \ln p_0' = -\lambda_e/RT_0 + c', \text{ and } \ln p'_0 = -\lambda_s/RT_0 + c'$$

$$\therefore \quad \ln \frac{p_s}{p_0'} = -\frac{\lambda_s}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right], \text{ and } \ln \frac{p_e}{p_0'} = -\frac{\lambda_e}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]$$

$$\therefore \quad \ln \frac{p_e}{p_s} = \frac{\lambda_s - \lambda_e}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right].$$

But $p_e = p_0$ = vapour pressure of supercooled solvent at C, $p_s = p$ = vapour pressure of solution at its freezing point, $\lambda_s - \lambda_e = \lambda_f$ = molecular heat of fusion,[1] hence

$$\ln \frac{p_0}{p} = \frac{\lambda_f}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right] = \frac{\lambda_f}{RTT_0}\,\delta T \quad . \; . \; . \quad [165]$$

[165] was deduced by Guldberg (1870, *loc. cit.*), who allowed for change of λ_f with temperature, neglected above on account of its small magnitude. If λ_f is in gm. cal., $R = 1{\cdot}987 = 2$ approx.

By combining [165] with [161] we find:

$$P/\rho L_f = \delta T/T_0 \quad . \; . \; . \; . \; . \; . \; . \quad [166]$$

---

[1] This relation is strictly true only at the triple point, at which the three phases co-exist at the same temperature and pressure (§ 89). In this case, if L_e, L_f, L_s are the latent heats of evaporation, fusion, and sublimation; v_l, v_s, v_g, the specific volumes of liquid, solid and vapour; p_0 the equilibrium pressure; and u_l, u_s, u_g the intrinsic energies, then:

$L_e = u_g - u_l + p_0(v_g - v_l)$; $L_s = u_g - u_s + p_0(v_g - v_s)$; $L_f = u_l - u_s + p_0(v_l - v_s)$. Hence, $L_s = L_e + L_f$. The value of L_f usually refers to $p = 1$ atm., but the value of $p(v_l - v_s)$ is so small compared with L_f that a fairly high pressure is required to produce any appreciable change.

where $L_f = \lambda_f/M$ and $\delta T = (T_0 - T)$ = depression of freezing point.

From [163]:

$$P = \delta T \,.\, 1000\rho L_f/24{\cdot}2T_0 \text{ atm.} \quad . \quad . \quad . \quad . \quad [167]$$

The experimental method of determining molecular weights by freezing points is due to Raoult.[1] The method at present in use was developed by Beckmann.[2]

Raoult expressed his results in terms of the *molecular depression*, Δ, for 1 mol of solute in 100 gms. of solvent.[3] The volume of the solvent is $100/\rho$, which may be taken as the volume of the dilute solution.

From [155a] and [165] we find:

$$(n/N) = (\lambda_f \delta T)/RTT_0 = \lambda_f \delta T/2TT_0 \text{ if } \lambda_f \text{ is in cal.}$$

For w gm. of solute in 100 gm. of solvent, if m is the molecular weight of the solute: $n = w/m$. If M is the molecular weight of the solvent: $N = 100/M$, hence:

$$wM/100\,m = \lambda_f \delta T/2TT_0 = \lambda_f \delta T/2T_0^2 \text{ approximately.}$$

Hence, since $L_f = \lambda_f/M$:

$$\delta T = 0{\cdot}02T_0^2 n/L_f \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [168]$$

where $n = w/m$ = number of mols of solute in 100 gm. of solvent.

If $n = 1$, δT = *molecular depression* Δ, hence:

$$\boldsymbol{\Delta = 0{\cdot}02T_0^2/L_f} \quad . \quad . \quad . \quad . \quad . \quad \mathbf{[169]}$$

Also
$$\Delta : \delta T = m : w \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [170]$$

from which m may be calculated if Δ has been determined for the solvent with a solute of known molecular weight.

[169] was deduced by van't Hoff in 1886.[4] It has been roughly verified for a number of substances by Eykman (1889).[5]

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[1] *A. C. P.*, 1880, **20**, 217, and many later papers; cf. his "Cryoscopie," Paris, 1901.

[2] *Z. p. C.*, 1888, **2**, 638, and later papers; cf. Stähler's "Arbeitsmethoden der anorg. Chem.," III., i., 100 ff. F. Flügel, *Z. p. C.*, 1912, **79**, 577; W. Roth, *ibid.*, 599; Adams, *J. A. C. S.*, 1915, **37**, 481; Bedford, *P. R. S.*, 1910, **83**, 454.

[3] It would be more logical to use 1 gm. of solvent here as well as in [159].

[4] Cf. *Z. p. C.*, 1887, **1**, 481; Ostwald's *Klassiker*, No. 110.

[5] *Z. p. C.*, 1889, **4**, 497.

Substance.	Δ.	$0{\cdot}02T_0^2/L_f$ obs.	T_0-273.	L_f obs.	L_f calc.
Water . .	18·58 [1]	18·5	0	79·63 [2]	78·75
Formic acid .	28	27·5	8	57·38	56·4
Acetic acid .	39	39·0	17	43·10	43·1
Stearic acid .	45	47·8	64	47·6	50·5
Benzene . .	51·2	51·9	5·4	29·9	30·3
p-toluidine .	53	51	42·1	39	37·5
Phenol . .	73	68·07	41·5	29·06 [3]	21·5
Benzophenone .	98	95	48·0	21·70 [3]	21·03

In the case of substances which polymerise or dissociate in solution, the osmotic pressure is given by : $P = icRT$, where i is *van't Hoff's factor*, related to the degree of association or dissociation a :— i = actual number of molecules present/number of molecules present on the assumption of no association or dissociation. With a binary electrolyte $i = 1 + a$, where a is the degree of electrolytic dissociation.

In this case we must write in instead of n in [155a], and :

$$\Delta = 0{\cdot}02inT_0^2/L_f \quad . \quad . \quad . \quad . \quad . \quad . \quad [171]$$

so that freezing point measurements provide a means of determining i.

The agreement, for very dilute solutions, among the values of i found by osmotic pressure, vapour pressure, and freezing point measurements is a necessary result of thermodynamics.[4]

EXAMPLES IX.

1. A closed vessel of 2 litres capacity contains initially 1 litre of water and 1 litre of air at 0° C. and 1 atm. The absorption coefficients at 0° C. are : O_2 0·04980 ; N_2 0·02388 ; A 0·05780. The composition of air in percentages by volume is N_2 78·06, O_2 21·00, A 0·94. The partial pressure of water at 0° is 4·58 mm. Find the partial pressures and the total pressure when the liquid is saturated.

2. The vapour pressure of mercury (mm.) at T° K is given (15°—270°) by $\log p = 15{\cdot}24431 - 3623{\cdot}932/T - 2{\cdot}367233 \log T$. Find the latent heat of evaporation per gm. at 100° C.

---

[1] Griffiths, quoted by Whetham, "Theory of Solution," 1902, p. 147.

[2] Dickinson, Harper and Osborne, *F.*, 1913, **176**, 453.

[3] Stratton and Partington, *P. M.*, 1922, **43**, 436.

[4] Depression of freezing point of fused salts, see Sackur, *Z. p. C.*, 1912, **78**, 550, 564 ; *ibid.*, 1913, **83**, 297. On the theory of freezing mixtures, see Porter and Gibbs, *P. M.*, 1922, **44**, 787.

3. The vapour pressures of alcohol at 30°, 40°, 70°, and 80° C. are 78·1, 133·4, 541, and 812 mm. Find the latent heat of evaporation at the boiling point 78·3° and compare with the measured value 205 gm. cal.

4. The vapour pressures of iodine at 0°, 15°, 30° and 55° C. are 0·03, 0·131, 0·469 and 3·08 mm. Find the latent heat of sublimation at 25° C.

5. A solution of 66 grams of camphor, $C_{10}H_{16}O$, in 1000 grams of ethyl alcohol C_2H_6O boils at 79·31°. The pure alcohol boils at 78·81°. Find the latent heat of evaporation of alcohol at its boiling point.

6. The latent heat of fusion of ammonia at − 75° C. is 1840 cals. per gm. molecule (Massol). Solutions of the alkali metals in liquid NH_3 are easily prepared; what would be the lowering of the F.P. of a solution of 3 gms. of sodium in 50 c.c. of liquid ammonia ? (Dens. NH_3 at − 75° C. = 0·7).

7. The density of benzene at its melting point is 0·8943 (5·4° C.), and its latent heat of fusion is 30·08 cals. per gm. By the addition of phenol the freezing point is lowered 0·54°. Calculate the osmotic pressure of the solution at 5·4° C., and its composition.

8. Show that if the latent heats of evaporation and sublimation are expressed in the form $\lambda_e = \lambda_0{}^e + (C_p - C_l)T$ and $\lambda_s = \lambda_0{}^s + (C_p - C_s)T$, where C_p, C_l, C_s are the molecular heats of the vapour, liquid, and solid, then :

$$\ln(p_0/p) = \frac{\Delta}{R}\left[\frac{\lambda_0{}^f}{T_0T'} - \frac{C_l - C_s}{2} \cdot \frac{\Delta t}{T'^2} + \frac{C_l - C_s}{3} \cdot \frac{(\Delta t)^2}{T'^3}\right]$$

where $\lambda_f = \lambda_0{}^f + (C_l - C_s)T$ is the molar heat of fusion; T_0, T' are the freezing points of pure solvent and solution, and $\Delta t = T_0 - T'$.

9. The lowering of the freezing point of a 1·9488 molar solution of KCl in water is 6·37° C. λ_f for water is 1435·5 cals. at 0° C., and the difference in the molecular heat capacities of ice and water is 9·04. If the vapour pressure of water is 17·539 mm. Hg at 20° C., calculate the vapour pressure of the KCl solution.

CHAPTER X

Entropy and Available Energy

58. Entropy.—In a simple Carnot's cycle: $Q_1/T_1 = Q_2/T_2$, or $Q_1/T_1 - Q_2/T_2 = 0$ (45). If we refer quantities of heat to the body undergoing the cycle, instead of to the reservoirs of heat, then Q_1 emitted by the source is absorbed by the body, and is positive, whilst Q_2 absorbed by the refrigerator is emitted by the body, and is negative. With this notation:

$$Q_1/T_1 + Q_2/T_2 = \Sigma Q/T = 0 \quad . \quad . \quad . \quad . \quad (172)$$

for the simple Carnot's cycle.

A more complex cycle, provided that the state of the system can always be represented by two variables, say p and v, may be split into a large number of very small adiabatic and isothermal changes, constituting a series of small Carnot's cycles (Fig. 25), to each of which (172) applies. The adiabatic parts of these small cycles which lie inside the loop representing the actual cycle cancel out in pairs in the limit, since each line is traversed twice, in opposite directions, but the isothermal parts make up the contour of the actual loop. Hence for the latter also we have the relation:

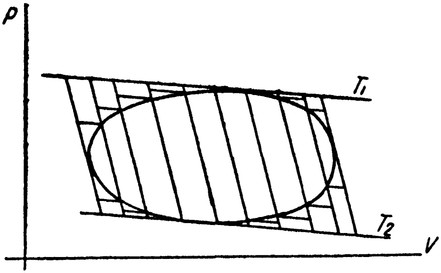

FIG. 25.

$$\Sigma Q/T = (\int) \delta Q/T = 0 \quad . \quad . \quad . \quad . \quad (173)$$

When the state of the system cannot be represented by two variables, the following method[1] may be used. Let a system M describe a reversible cycle, and let the heat received by M at temperature T at any stage of the cycle, be δQ. δQ may be supplied from a *reversed* Carnot's engine working with a gas, to which the above proof applies. The engine has the system M as source, and a large reservoir of heat at the constant temperature T_0 as refrigerator. The heat abstracted from the latter will be, in the stage in question, $\delta Q' = T_0 \delta Q/T$, and the total amount of heat abstracted during the cycle is $Q_0 = T_0 (\oint) \delta Q/T$.

---

[1] G. H. Bryan, "Thermodynamics," § 75.

All bodies have returned to the initial state, except possibly the reservoir at T_0; hence Q_0 cannot be positive, since then an equivalent amount of work must have been done, which contradicts the Second Law. And since the cycle is reversible, Q_0 cannot be negative, because it could be made positive by simply reversing the cycle, which gives the first case. Hence Q_0 must vanish : $\therefore (\oint) \delta Q/T = 0$, as before.

This result was obtained by Clausius [1] and Lord Kelvin.[2]

For an *isothermal reversible cycle :*

$$1/T \,.\, (\oint)\delta Q = 0 \quad \therefore \quad (\oint) \delta Q = 0, \text{ which is equation (44a).}$$

Now cut the cycle into two parts (Fig. 3, § 9), and integrate $\delta Q/T$ along each :

$$(\oint)\frac{\delta Q}{T} = \int_{M\,A}^{B}\frac{\delta Q}{T} + \int_{N\,B}^{A}\frac{\delta Q}{T} = 0 \quad \therefore \quad \int_{M\,A}^{B}\frac{\delta Q}{T} = \int_{N\,A}^{B}\frac{\delta Q}{T}.$$

Thus $\delta Q/T$ must be *a perfect differential* of some function S, the change of which does not depend on the particular *reversible* path along which the system is conveyed from state A to state B.

If a system or part of a system at the absolute temperature T absorbs a quantity of heat δQ, the quotient $\delta Q/T = dS$ is called the increase of *entropy* (Greek ἡ τροπή, *change*) of the system due to this absorption of heat.[3]

If A and B are two states of a system which can be connected by a series of *reversible* changes, the increase of entropy of the system in passing from the state A to the state B is defined by the expression :

$$\int_A^B \frac{\delta Q}{T} = S_B - S_A \quad . \quad . \quad . \quad . \quad . \quad (174)$$

the integral being taken along the reversible series of changes.

---

[1] *A. P.*, 1854, **93**, 481.

[2] *Trans. R. Soc. Edin.*, 1854, **21**, 123.

[3] The name is due to Clausius, *A. P.*, 1865, **125**, 390; *ibid.*, 1854, **93**, 481; *P. M.*, 1856, **12**, 81, 241.

The change of entropy of the body or system will *always* be $S_B - S_A$, as defined above, whether the *actual* change from A to B is reversible or irreversible, since the entropy of the body depends on its actual state alone, but if this change is *irreversible* the value of $S_B - S_A$ will not be $\int_A^B \delta Q'/T$, where $\delta Q'$ denotes an element of heat absorbed in the irreversible change.

We may now compare the *results of the First and of the Second Laws :*

First Law (equation 10): $\int_A^B (\delta Q - \delta A) = U_B - U_A$ for *all* changes, reversible or irreversible.

Second Law (equation 174): $\int_A^B \frac{\delta Q}{T} = S_B - S_A$, for reversible changes only.

If *unit mass* of a homogeneous substance is heated reversibly under specified conditions the increase of entropy is

$$s_2 - s_1 = \int \delta Q/T = \int c dT/T \quad . \quad . \quad . \quad . \quad (174a)$$

where c is the specific heat under the specified conditions. Hence

$$\partial s/\partial T = c/T \quad . \quad . \quad . \quad . \quad . \quad \mathbf{(174b)}$$

If *unit mass* of a homogeneous substance is converted by absorption of heat into another state of aggregation, the increase of entropy is

$$s_2 - s_1 = \int \delta Q/T = (1/T)\int \delta Q = L/T \quad . \quad . \quad \mathbf{(174c)}$$

where L is the *latent heat* of the given change of state.

59. **Maximum Work.**—*A process yields the maximum amount of work when it is conducted reversibly.* The truth of this statement (cf. § 26) may be seen by considering a number of actual cases.

(1) *The expansion of a gas* may be conducted :

(*a*) *Reversibly*, by allowing the gas to expand in a cylinder under a piston as in § 23. If the gas is ideal, the isothermal change of volume from V_1 to V_2 at temperature T will furnish work RT ln (V_2/V_1) per mol (§ 36), the *maximum work* for the isothermal change.

(*b*) *Irreversibly*, when the gas contained in a vessel of volume V_1 is put in connection with a vacuous vessel so that the combined volumes are V_2. The gas will rush into the vacuum without the performance of external work. The temperature will remain constant, by Joule's law (§ 33), so that this is a case of irreversible isothermal expansion.

Between case (*a*) and case (*b*) we may imagine intermediate changes, in which the work is always less than the maximum obtained in the reversible change (*a*).

(2) *Passage of heat from a warmer to a cooler body.* If a hot body is put in thermal contact with a cooler body heat passes by conduction and no work is obtained. This heat might have been transferred by a Carnot's engine working between the two bodies as source and refrigerator, and if the absolute temperatures are T_1 and T_2, an amount of work $Q_1(T_1 - T_2)/T_1$ is obtained when Q_1 is taken from the hot body, and $Q_2 = Q_1 - [Q_1 (T_1 - T_2)/T_1] = Q_1 . T_2/T_1$ given up to the cooler body. With transfer by conduction the possibility of obtaining this work is lost.

60. The Principle of Dissipation (Degradation) of Energy.—As a result of the considerations of § 59 we may assume that *in all irreversible processes the work obtained is less than the maximum possible.* All irreversible processes are said to be attended by *dissipation of energy* (to *dissipate* = to squander, disperse, or waste, not destroy) from a more useful into a less useful form. Work is the most useful form, and where energy which *could* have been recovered as work is not, it is dissipated (degraded) to a less useful form, which may be (and usually is) heat in a body, as in example (2) in § 59, but not necessarily, as in Example (1*b*). That heat in a body at a uniform temperature is completely unavailable for conversion into work unless a lower temperature is at our disposal follows from the Second Law (§ 26), and Lord Kelvin, who introduced the ideas of available and unavailable energy and dissipation of energy in 1852,[1] pointed out that the final result of the innumerable irreversible changes taking place would be the reduction of the whole stock of energy in the " universe " into heat at a uniform temperature. All change would then cease.

Available energy may be defined as that which is completely convertible into useful work by reversible processes. From this point of view, different forms of energy are classified according to their *practical* value as sources of work; the energy of a raised weight, for example, represents a distribution of energy which is immediately available for conversion into work; a quantity of heat in a body is either not at all, or only partially available, with bodies at finite temperatures.

[1] *P. M.*, 1852, **4**, 304; 1853, **5**, 102.

61. Entropy and Available Energy.—The maximum work obtainable from heat Q_1 taken from a body of fixed composition and volume at the temperature T_1 is (46):

$$A = Q_1 - Q_2 = Q_1 (1 - T_2/T_1)$$

where T_2 is the lowest temperature available for the refrigerator of a reversible engine. The balance of Q_1, viz., $Q_2 = Q_1T_2/T_1$, is *unavailable energy*, given up as heat to the refrigerator. It is proportional to the lowest available temperature and inversely proportional to the temperature of the body from which Q_1 is taken. Q_1/T_1 is the *entropy* of the quantity of heat Q_1 at T_1, hence: *entropy = unavailable energy divided by the lowest available temperature.* Entropy and unavailable energy must increase together; *increase of entropy* means *diminution of available energy*, or *dissipation of energy.*

But (§ 60) *spontaneous changes* are attended by decrease of available energy, hence by increase of entropy, ∴ *all change should cease when the available energy of a system is a minimum, or the entropy a maximum* (see § 69).

62. Free Energy.—It is not always necessary to have a difference of temperatures to obtain part of the intrinsic energy of a system in the form of useful work, but the state of the system must then change. *Energy available at constant temperature is called Free Energy,* which we denote by F.

Thus, in the isothermal reversible expansion of a gas, work may be obtained in unlimited quantities. In this case the work comes from the heat absorbed from outside by the gas, which is rendered available, provided the gas can expand into a region of lower pressure. After the expansion, however, the state of the gas is altered; its volume has increased, and it is not possible to repeat the process. To bring the gas back to the initial state an equal amount of work must be spent in its compression, and this is emitted as useless heat into the surroundings.

Again, when zinc dissolves in acid it evolves heat. But if the zinc is dissolved reversibly in a galvanic cell, electrical energy, which is convertible into useful work without residue, may be obtained. The state of the system is again changed, and it is not possible to repeat the process without reducing the zinc from the solution, which involves expenditure of useful energy.

Energy unavailable in isothermal changes has been called *Bound Energy.* The sum of the free and bound energy changes is equal to the intrinsic energy change. In irreversible processes free energy is converted into bound energy. Increase in bound energy corresponds with absorption of *latent heat*, but this is not confined to changes of state. A reversible galvanic cell may operate immersed in a large thermostat, so that the temperature remains constant. The free energy change may be utilised in the form of electrical energy, but the cell, even when working reversibly, will in general absorb or emit heat. The existence of this latent heat of a galvanic cell was clearly described by Hemholtz (§ 76). If the cell drives a finite current through a resistance immersed in the bath, there will, in addition to the reversible latent heat transfer, be heat given out to the bath from the resistance, and the free energy output is reduced by an equivalent amount.

In isothermal reversible changes the maximum work done will be equal to the diminution of free energy :

$$A_T = F_1 - F_2 = - \Delta F \quad . \quad . \quad . \quad . \quad (175)$$

This follows from the definition of free energy, *i.e.*, available energy in isothermal changes.

If the change is small :

$$\delta A_T = - dF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (176)$$

The fact that dF is a perfect differential follows from (44), since the work done in an isothermal reversible change, *i.e.*, the diminution of F, is independent of the way in which the change from the initial to the final state is carried out. The free energy of a system, therefore, depends only on the actual state of the system. If a system in state A is converted isothermally into the state B, the diminution of free energy of the system is always $F_A - F_B$, but it is only when the change is reversible that $F_A - F_B$ is equal to A_T, the work done in the change. In irreversible changes the Principle of Dissipation of Energy states that the work is then less than the maximum amount, A_T, so that in irreversible changes we have, instead of equation (176), the inequality :

$$\delta A_T < - dF \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (177)$$

Exercise.—Interpret the inequality $- \delta A_T > dF$.

We may again compare the equations representing the First and Second Laws of Thermodynamics :

First Law : $Q_v = U_1 - U_2$ for *all* changes.

Second Law : $A_T = F_1 - F_2$ for *isothermal, reversible,* changes only.

The properties of the free energy are much more difficult to understand than those of the intrinsic energy. In Example (1*a*) of § 59, for example, the whole of the diminution of free energy of the gas is derived from energy outside the gas itself. The free energy was first used by Gibbs in 1875[1]; important applications of it were made by Helmholtz in 1882.[2]

63. Irreversible Changes.—The facts of experience that:

(1) Every process which can take place spontaneously may, if reversibly conducted, be made to yield useful work;

(2) Every spontaneous process is irreversible;

led us to the *Principle of Dissipation of Energy*,[3] [illegible] to which every spontaneous change leads to dissipation of energy. It is very difficult to give a formal proof of this from the two laws of Thermodynamics, yet it cannot be a separate law, since an application of the two laws of Thermodynamics shows that the principle of dissipation of energy is true *in every particular case* considered. Heat flows from warmer to colder localities; gases tend to mix and do not unmix spontaneously, and so on. In each case it can be shown that there is loss of possible work, *i.e.*, dissipation of energy. If we assume the principle to be true we can predict to some extent the direction of a spontaneous change, since it must be one attended by dissipation of energy. If we can calculate the available energy of two states of a system as functions of state, we can say that a state tends to pass spontaneously into another with less available energy. Thus, it can be shown that the free energy of a mixture of gases is less than the sum of the free energies of the unmixed gases at the same temperature and pressure (§ 64). If, therefore, the separate gases are put in contact, we should expect them to mix by some process which will be attended by dissipation of energy, and the gases do in fact mix by diffusion. Once they are mixed they do not separate again, since this would mean that the available energy had increased by a spontaneous process, in contradiction to the principle of dissipation.

It is possible to mix the gases reversibly with performance of useful work. The equivalent of this work will be dissipated in spontaneous mixing, but the diminution of free energy of the gases is the same whether they are mixed reversibly or irreversibly, since the free energy depends only on the actual state of the system.

64. Reversible Mixing of Ideal Gases.—The reversible mixing of gases is effected by means of selectively permeable septa (see § 53). Each gas exerts pressure on a septum impervious to it, but not on a septum which it permeates freely.

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[1] *Scient. Papers*, i., 87.

[2] Ostwald's *Klassiker*, No. 124.

[3] Lord Kelvin, *P. M.*, 1852, 4, 304; 1853, 5, 102; *Proc. Roy. Soc. Edin.*, 1898, 22, 126.

Let 1 mol of gas [1] be separated from 1 mol of gas [2] in the cylinder shown in Fig. 26 by means of the two selectively permeable pistons A (freely permeated by [1] but impervious to [2]), and B (freely permeated by [2] but impervious to [1]). The pistons tend to separate, A under the pressure exerted by gas [2], B under the pressure exerted by gas [1]. If the expansive forces are balanced by thrusts applied to the piston rods, and the whole apparatus is immersed in a large bath at temperature T, mixing may be carried out isothermally and reversibly. By pressing in the pistons, the gas mixture formed will be separated reversibly into its constituents.

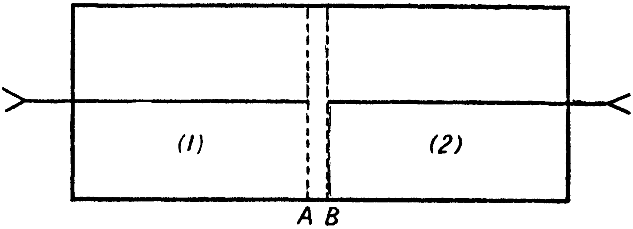

FIG. 26.

If there are n_1 mols of the gas [1] and n_2 mols of the gas [2], the *work done in mixing the gases* will be :

$A_1 = n_1 RT \ln (v_1 + v_2)/v_1$ for the gas [1] expanding from volume v_1 to the total volume $v_1 + v_2$;

$A_2 = n_2 RT \ln (v_1 + v_2)/v_2$ for the gas [2] expanding from volume v_2 to the total volume $v_1 + v_2$.

The *total work* will be

$$A = A_1 + A_2 = RT\left[n_1 \ln \frac{v_1 + v_2}{v_1} + n_2 \ln \frac{v_1 + v_2}{v_2}\right]. \quad [178]$$

If $n_1 = 1$, $n_2 = 1$, then $v_1 = v_2$, and $A = 2RT \ln 2$.

Work done by the reversible mixing of gases is positive, hence the *free energy* of the mixture is less than the sum of the free energies of the separate gases. Mixing is therefore a spontaneous process, since it is attended by dissipation of energy when the gases mix without doing work. Conversely, to unmix gases which have mixed spontaneously by diffusion will require expenditure of work. No *intrinsic energy* change occurs in the gases, since the intrinsic energy of an ideal gas depends only on temperature, and no heat is evolved or absorbed when ideal gases mix without chemical action. The equivalent of the work obtained in reversible mixing of gases must therefore have been absorbed as heat from the environment, and the equivalent of work spent on unmixing gases must have been emitted as useless heat to the environment at the same temperature as the gases. In the latter case, with equimolar amounts of gases, an amount $2RT \ln 2$ of useful work is dissipated by conversion into heat.[1]

65. **Maxwell's Demons.**—We can imagine the unmixing of a gas mixture carried out without dissipation of energy if we have the services of a *being* which can deal with individual molecules. Such a being, imagined by Maxwell,[2] is usually called a *demon* (= intelligence). Let the mixture be divided into two parts by a partition provided with a door, and let a demon be stationed at the door. All molecules of gas [1] passing in one direction are to be allowed to pass through the door, and all the molecules of the gas [2] allowed to pass the opposite way. Molecules approaching the door in wrong directions must not pass, but rebound off the closed door. The molecules are assumed perfectly elastic, and in motion, in accordance with the kinetic theory of gases. The mixture is thus separated into gases [1] and [2] without expenditure of work.

Again, with the apparatus filled with a single gas, if the demon lets through fast molecules in one direction and slow molecules in the other direction, the gas will separate into a hotter and a cooler part. It is assumed that fast molecules correspond with higher temperatures and slow molecules with lower temperatures, and that in a gas which seems to be uniform in temperature to a thermometer the molecules have all possible velocities, in accordance with the kinetic theory of gases. If the junctions of a thermocouple are immersed in the two halves of the vessel, an electric current will be produced, and useful work can be obtained from it. Thus, from a system initially at a uniform temperature, work has been obtained.

The above results are, of course, in contradiction to the Second Law of Thermodynamics. This cannot be true in the same sense as the First Law, but is only *statistically true*; it holds for matter in the *aggregate* but not necessarily for individual molecules. It can be violated by *imaginary* apparatus capable of controlling the motions of individual molecules, or the *microscopic state* of the system, but not by actual apparatus capable of controlling only the system in bulk.[3]

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[1] Lord Rayleigh, *P. M.*, 1875, **49**, 311; Gibbs, 1875, "Scient. Papers," i., 166; Nernst, "Theoretische Chemie," 1893.

[2] "Theory of Heat," 1897, p. 338.

[3] See, especially, Smoluchowski, "Vorträge über die kinetische Theorie der

It is evident that insight into the Second Law might be obtained from molecular theory, and in the application of the theory of statistics to such a dynamical system as a gas illuminating information has been obtained by Boltzmann, Gibbs, and Planck. This *Statistical Mechanics* is, however, a science outside the compass of pure thermodynamics (cf. § 68).

66. Law of Consecutive Reactions.—Suppose that an initial system A has a free energy F_A, and let it be possible to derive from A the different systems B, C, D, . . ., for all of which the free energies F_B, F_C, F_D, . . . can be calculated. We now enquire what will occur when the system A is left to itself.

Any change will be *possible* for which the free energy decreases. If $F_B < F_A$; $F_C < F_A$; $F_D > F_A$, then changes $A \rightarrow B$ and $A \rightarrow C$ are both possible, but change $A \rightarrow D$ is not possible. We can definitely assert that $A \rightarrow D$ will not occur spontaneously. But if $F_A - F_B > F_A - F_C$, which of the two possible changes $A \rightarrow B$ and $A \rightarrow C$ will take place spontaneously? The answer is that we cannot tell whether either will actually take place. For instance, diamond in presence of oxygen gas may not pass into carbon dioxide, although this change would involve a diminution of free energy, unless the system is first heated.[1] The first system is said to be retained in its state by *passive resistances*. Again, the burning of diamond to carbon dioxide involves a greater diminution of free energy than the burning to monoxide, yet the former change does not occur completely unless a catalyst, such as moisture, is present. In fact, the change which actually occurs in a system is rarely one involving the *maximum* diminution of free energy, but one involving the minimum, and the system then changes into the final state in stages.[2] A familiar example is the action of chlorine on a solution of caustic soda. The stable state is sodium chloride + oxygen, but the first product is partly hypochlorite, and this may change into chlorate. The latter passes into chloride and oxygen only at high temperatures, or in presence of catalysts. A *catalyst* is something which removes in some at present unknown way the passive resistances in a system.

It will be noted that, although the principle of dissipation of energy tells us definitely which changes will *not* take place spontaneously, it gives us no information as to which of the possible changes will take place, if at all, under given conditions. It is

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Materie und der Elektrizität" (various authors), Teubner, 1914, 89 ff.; Planck, "Acht Vorlesungen über theoretischen Physik," 1910, 50 ff.

[1] The unverified assumption that in such cases extremely slow changes do occur does not appreciably modify the discussion.

[2] G. D. Liveing, "Chemical Equilibrium," Cambridge, 1885; Ostwald, *Lehrb.*, II., i., 512.

hardly likely that the additional information which would decide such questions will ever be found.

67. Irreversible Changes.—It can be shown that in each separate case of irreversible change there is dissipation of energy, or increase of entropy, and it may safely be *assumed* that the law is applicable to *all* irreversible changes, *i.e.*, all which actually occur in Nature.

Planck[1] has conceived the matter from a rather different standpoint. Processes occur in Nature in one definite sense. Heat passes from hotter to colder bodies, liquids and gases mix and do not unmix, and so on. If, therefore, there is any fundamental difference between reversible and irreversible processes it may be associated with uniform change of some magnitude characteristic of the state of the system, and connected with change of state in a particular way. Since, in a large number of separate cases it may be shown that there is increase of entropy, or decrease of available energy, it may be assumed that these are characteristic of all real, *i.e.*, irreversible, changes.

68. Alternative Forms of the Second Law of Thermodynamics.—When a system contains bodies at different temperatures the most convenient form of the Second Law is that given by Lord Kelvin[2]: *It is impossible to obtain work by cooling a body below the lowest temperature in the system.*

The consideration of refrigeration in § 28 leads to the form of the Second Law adopted by Clausius[3]: *Heat cannot of itself,* i.e., *without compensation, pass from a colder to a hotter body.*

By making use of a reversible heat engine it can be shown that these two, and the form adopted in § 26, are merely equivalent statements of the same law.

In the form given by Clausius, the Second Law is not so strikingly contradicted by the considerations on Maxwell's demons (§ 65), since the work is still obtained at the expense of the "hot" molecules, *i.e.*, those with greater kinetic energies. It is impossible, of course, to speak of the "temperature" of an isolated molecule in free space, but a single molecule in an enclosure may have a temperature.[4]

A great advance was made in the direction of the physical interpretation of entropy, and the systematisation of irreversible processes, when Ludwig Boltzmann (1877), following a suggestion of Gibbs, showed that the definition of entropy could be regarded as a problem in the theory of probabilities.[5] The Second Law and irreversibility depend not so much on peculiarities of molecular motions which constitute heat as on the impossibility of outward control of enormous numbers of molecules in material bodies. The kinetic energies of these molecules cannot be directed into any sort of united effort in one direction, but are diffusely dissipated throughout the mass of the gas. The energy of a gas tends spontaneously to become diffused in this way, and at the same time the entropy increases. The entropy of a system is then, from this point of view, a measure of what Gibbs called the " mixed-upness " of the system.

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[1] "Thermodynamik," 3 Aufl., pp. 82 ff.

[2] *P. M.*, 1852, 4, 13.

[3] *A. P.*, 1854, 93, 488; *P. M.*, 1856, 12, 86.

[4] Planck, *B. B.*, 1916, p. 653.

[5] "Wiss. Abhl.," II., 164; "Gastheorie," II., 253 ff.

According to Boltzmann, the entropy S depends on what he calls the *probability* P of the state, by the simple relation [1]:

$$S = k \ln P$$

where k is a universal constant, $k = R/N_0$, where N_0 = Avogadro's constant. The assumption that there is no additive constant, made by Planck, is equivalent to Nernst's theorem (§ 124), and is in agreement with the quantum theory.[2]

The probability P defines the probability of the system as compared with a system in which the co-ordinates of all the molecules have the same mean value.

69. Isothermal Changes.—The *heat absorbed in any isothermal reversible* change is (§ 58):

$$Q = \int \delta Q = \int T dS = T \int dS$$

In this case Q depends only on the initial and final states, and $\delta Q = dQ$ is a perfect differential.

The *work done* is:

$$A = \int \delta Q - \int dU = \int \delta Q - (U_2 - U_1) \quad \text{(general case)};$$

$$A = \int T dS - (U_2 - U_1) \quad \text{(reversible changes)};$$

$$A_T = T(S_2 - S_1) - (U_2 - U_1) \quad \text{(isothermal reversible changes).}$$

Hence A_T in this case depends on the initial and final states only, and $\delta A_T = dA_T$ is a perfect differential. The last equation may be rearranged:

$$A_T = (U_1 - TS_1) - (U_2 - TS_2) \quad . \quad . \quad . \quad (179)$$

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[1] Boltzmann's equation has an additional additive constant: cf. Planck, " Wärmestrahlung," 4th ed., p. 119.

[2] Planck, " Theorie der Wärmestrahlung," 1921, pp. 111–133; J. W. Gibbs, " Elementary Principles in Statistical Mechanics," 1902; Jeans, " Dynamical Theory of Gases," 1921; Sackur, *A. P.*, 1911, **37**, 958.

so that the maximum work done in isothermal changes can be represented as the difference between the values of the function (U − TS) for the initial and final states.

The maximum work in this case is defined as the diminution of free energy (§ 62), hence:

$$\mathbf{F = U - TS} \quad . \quad . \quad . \quad . \quad . \quad . \quad \mathbf{(180)}$$

For a small isothermal reversible change $\delta A_T = -dF$, but if the change is irreversible: *work done* $< \delta A_T < -dF$, by the principle of dissipation of energy, hence:

$$\delta Q - dU \leqq TdS - dU\,;\ \delta Q \leqq TdS\,;\ \delta Q/T \leqq dS \quad . \quad (181)$$

the equality referring to reversible, and the inequality to irreversible, changes. Relation (181) shows that in irreversible changes the heat absorbed by the system is less than corresponds with the increase of entropy, hence in such cases entropy is generated in the system itself, *i.e.*, irreversible changes lead to increase of entropy.

We have assumed, however, that actual changes are irreversible, hence the condition for equilibrium is that no irreversible changes can occur. This is the case when either (i.) the free energy is a minimum, or (ii.) the entropy is a maximum. States of *true equilibrium* are alone considered, in which a small change of external conditions leads to a small displacement of the equilibrium state.

70. Differential Equations.—The fundamental equation for the reversible change of state of a system defined by two independent variables is, for *unit mass*:

$$du = \delta Q - \delta A = Tds - pdv.$$

Take v and s as independent variables, then:

$$(\partial u/\partial s)_v = T \text{ and } (\partial u/\partial v)_s = -p \quad . \quad . \quad . \quad (182)$$

Take v and T as independent variables, and put $u - Ts = f$, then:

$$df = du - Tds - sdT = -sdT - pdv$$

$$\therefore \quad (\partial f/\partial T)_v = -s \text{ and } (\partial f/\partial v)_T = -p \quad . \quad . \quad (183)$$

Take p and T as independent variables and put $u - Ts + pv = z$, then:

$$dz = du - Tds - sdT + pdv + vdp = -sdT + vdp, \text{ hence:}$$

$$(\partial z/\partial T)_p = -s \text{ and } (\partial z/\partial p)_T = v \quad . \quad . \quad . \quad (184)$$

The function z is called the *thermodynamic potential* (see § 71).[1]

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[1] First used by Gibbs in 1875: "Scient. Papers," I., 87.

Take s and p as independent variables and put $u + pv = h$, then:

$$dh = du + pdv + vdp = \mathrm{T}ds + vdp, \text{ hence:}$$

$$(\partial h/\partial s)_p = \mathrm{T} \text{ and } (\partial h/\partial p)_s = v \quad . \quad . \quad . \quad (185)$$

Differentiate the first equation of (182) with respect to v and the second with respect to s, and put $\partial^2 u/\partial s\partial v = \partial^2 u/\partial v\partial s$ (du is a perfect differential; *H. M.*, § 57)

$$\therefore \quad (\partial \mathrm{T}/\partial v)_s = -(\partial p/\partial s)_v \quad . \quad . \quad . \quad . \quad . \quad (182a)$$

Similarly:

$$(\partial s/\partial v)_{\mathrm{T}} = (\partial p/\partial \mathrm{T})_v \quad . \quad . \quad . \quad . \quad . \quad . \quad (183a)$$

$$(\partial s/\partial p)_{\mathrm{T}} = -(\partial v/\partial \mathrm{T})_p \quad . \quad . \quad . \quad . \quad . \quad (184a)$$

$$(\partial \mathrm{T}/\partial p)_s = (\partial v/\partial s)_p \quad . \quad . \quad . \quad . \quad . \quad . \quad (185a)$$

Equations (182a) to (185a) are known as *Maxwell's Relations*.[1]

71. Thermodynamic Potential.—For a small reversible isothermal change the work done is equal to the diminution of free energy: $\delta \mathrm{A_T} = -d\mathrm{F}$, hence:

$$(d\mathrm{F} + \delta \mathrm{A})_{\mathrm{T}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (186)$$

This is a condition of equilibrium at constant temperature, since if only reversible changes can occur the system is necessarily in equilibrium.

If the external work is $\delta \mathrm{A_T} = pd\mathrm{V}$, then:

$$(d\mathrm{F} + pd\mathrm{V})_{\mathrm{T}} = 0$$

hence, if $d\mathrm{V} = 0$, *i.e.*, if the volume is also constant:

$$(d\mathrm{F})_{\mathrm{V,\,T}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (187)$$

This is the condition of equilibrium at constant temperature and volume.

Let $d\mathrm{F} + \delta\mathrm{A} = d\mathrm{Z}$. Under what conditions can $d\mathrm{Z}$ be a differential of a function Z? Obviously when A depends only on the initial and final states, since F has that property. A case in which A depends only on the initial and final states is when the pressure is constant:

$$\mathrm{A} = p(\mathrm{V}_2 - \mathrm{V}_1).$$

Thus, if $\mathrm{Z} = \mathrm{F} + p\mathrm{V} = \mathrm{U} - \mathrm{TS} + p\mathrm{V}$

$$d\mathrm{Z} = d\mathrm{F} + pd\mathrm{V} + \mathrm{V}dp,$$

and if p is constant ($dp = 0$): $d\mathrm{Z} = d\mathrm{F} + pd\mathrm{V}$.

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[1] "Theory of Heat," 1897, pp. 165 ff.—geometrical proofs. See Lunn, *P. R.*, 1920, **15**, 269; Bridgman, *ibid.*, 1914, **3**, 273.

The condition of equilibrium at constant temperature (186) then gives the condition of equilibrium at constant temperature and pressure :

$$(dZ)_{p,\,\mathrm{T}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (188)$$

Z is called the [illegible] *potential* (Lat. *potentia* = power, or force), by analogy with the potential function in dynamics :

$$\phi_1 - \phi_2 = \text{work}.$$

We have also for reversible changes $dS - \delta Q/T = 0$, *i.e.*,

$$dS - (dU + pdV)/T = 0 ;$$

hence the condition of equilibrium when the energy and volume are constant ($dU = 0$, and $dV = 0$) is :

$$(dS)_{\mathrm{V},\,\mathrm{U}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (189)$$

Since all reversible changes are characteristic of equilibrium states, and all changes in which the available energy increases or the entropy diminishes are impossible changes, the *general* conditions of equilibrium may be written in the form :

$$(\delta F)_{\mathrm{V},\,\mathrm{T}} \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (190)$$

$$(\delta S)_{\mathrm{V},\,\mathrm{U}} \leqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (191)$$

$$(\delta Z)_{p,\,\mathrm{T}} \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (192)$$

The changes indicated by the equalities are reversible ; those by the inequalities are impossible.

All these relations have been deduced from the principle of dissipation of energy. The last relation follows from the fact that *the change of thermodynamic potential is the available energy change corrected for the external work.* For when p is constant :

$$-\Delta Z = -\Delta F - p\Delta V$$

$$\therefore \qquad -\Delta Z = A_{\mathrm{T}} - p\Delta V = A_{\mathrm{T}}' \quad . \quad . \quad . \quad . \quad (193)$$

The work done, *minus* the work done by change of volume under the constant external pressure, is equal to the diminution or thermodynamic potential. $-\Delta Z$ is a measure of the *electrical, chemical* or *internal* work done by a system at constant pressure.

72. Stability of Equilibrium.

We distinguish in statics between *three types of equilibrium : stable, unstable,* and *neutral.* The first is typified by a cone resting on its base, the second by a cone resting on its point, and the third by a cone resting on its side. The essential difference between the three cases is the behaviour of the system to *small* displacements from the position of equilibrium. In stable equilibrium the potential energy of the system increases on small displacement (since the centre of gravity is raised); in unstable equilibrium the potential energy decreases on small displacement (since the centre of gravity is lowered); whilst in neutral equilibrium the potential energy remains constant (since the vertical position of the centre of gravity remains constant). The three cases are characterised by the existence of *a minimum, a maximum, and a stationary value, of the potential energy*, respectively.

The potential energy of statics is evidently a special case of the available energy of thermodynamics, when thermal changes are excluded, and the generalisation of the above result (known as *Dirichlet's theorem*) is that *the stable state of a system is one in which the available energy is a minimum :*

$$(\delta^2 F)_{V,\,T} > 0, \text{ and } (\delta^2 Z)_{p,\,T} > 0 \quad . \quad . \quad . \quad . \quad . \quad (194)$$

To these we may add the condition that the entropy shall be a maximum :

$$(\delta^2 S)_{V,\,U} > 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (194a)$$

An example of a state of neutral equilibrium is furnished by a liquid in contact with its saturated vapour. In this case a small increase in volume of the system leads to the production of a further small quantity of vapour and the pressure remains constant. The change of Z is zero. An example of stable equilibrium is a gas under its equilibrium pressure. Small changes of outside pressure produce small isothermal or adiabatic changes of volume, but the original volume is restored along with the original outside pressure. An example of unstable equilibrium is a superheated liquid, which boils explosively on reduction of outside pressure.[1]

F. Massieu [2] first showed that *all* characteristic properties of fluids can be expressed in terms of one or other of two functions, or their differential coefficients :

$$H = -(U - TS)/T[= -F/T]\,;\; H' = -(U - TS + pV)/T[= -Z/T],$$

which he called, for unit mass, the *characteristic functions* of the fluid. Planck later used the second as a potential function, denoted by ϕ, which has the same properties in a system at constant temperature and pressure as the entropy at constant energy and volume.

Maxwell [3] observed that the maximum work of an isothermal process could be represented as the diminution of a function U — TS, which he called, in 1875, the *available energy*, a name proposed by Gibbs in 1873.[4] Gibbs also used the function U — TS + pV, and in a later memoir [5] three functions : $\psi = U - TS$; $\zeta = U - TS + pV$; $\chi = U + pV$, which he called the *force function for constant temperature*, the *force function for constant pressure*, and the *heat function for constant pressure*, respectively. These are our F, Z, and H. (He used ϵ for U, η for S, and t for T.)

In 1879 Lord Kelvin [6] used the term *motivity* for " the possession, the waste of which is called dissipation " ; at constant temperature this is identical with Maxwell's available energy, or Gibbs's ψ.

In 1882 Helmholtz generalised the potential energy function of mechanics so as to obtain a function which, at a given temperature, should represent the maximum obtainable work for a change of configuration, and could be transferred to other temperatures by means of the Second Law of Thermodynamics. He called this the *free energy*. It is our F.

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[1] On stability of equilibrium, cf. Duhem, " Mécanique chimique " ; Gibbs, " Scientific Papers," Vol. I. ; van der Waals-Kohnstamm, " Lehrbuch der Thermodynamik."

[2] *J. P.*, 1869, **4**, 216.

[3] " Theory of Heat," 1871.

[4] " Scientific Papers," I., 33.

[5] 1878, *ibid.*, 87–92.

[6] *P. M.*, 1879, **7**, 348.

Maxwell,[1] in discussing the work of Gibbs (which he was practically the first to notice), remarked that the existence of a system depends on the magnitudes of the system, which are: the quantities of the components, the volumes, the entropies, as well as on the intensities of the system, viz., the temperature and the potentials of the components. In his "Theory of Heat" (1897, p. 194) he also refers to the separation of the variables defining the state of the system into two sets, one of which includes intensities (pressure, temperature), and the other magnitudes (volume, entropy). These are our generalised intensities and generalised co-ordinates, respectively (§ 74).

73. Specific Heat of Saturated Vapour. The Critical Point.

Let unit mass of a mixture of m parts of vapour in equilibrium with $(1 - m)$ parts of liquid be contained in a vessel at a temperature T. Let the temperature be raised to $T + dT$ and let a further small quantity dm of vapour be produced, the pressure being changed to the saturation pressure at $T + dT$. The amount of heat absorbed in raising the temperature of unit mass of vapour 1°, *the pressure at the same time being raised so as to preserve the substance in the saturated state*, is called the *specific heat of saturated vapour*, *h*. If c is the specific heat of the liquid under these conditions the heat absorbed in the above change is:

$$\delta Q = L_e dm + \{ c(1 - m) + hm \} dT$$

$$\therefore \quad (\partial s/\partial m)_T = L_e/T \text{ (cf. 174c)}$$

$$(\partial s/\partial T)_m = \{c(1 - m) + hm\}/T.$$

Since ds is a perfect differential: $\partial^2 s/\partial m \partial T = \partial^2 s/\partial T \partial m$,

$$\therefore dL_e/dT = h - c + L_e/T \quad . \quad . \quad . \quad . \quad . \quad (195)$$

In the case of water at 100° C., $c = 1{\cdot}01$; $L_e = 538{\cdot}7$; $dL_e/dT = -0{\cdot}61$; $T = 373 \therefore h = 1{\cdot}01 - 0{\cdot}61 - 1{\cdot}44 = -1{\cdot}04$. The specific heat of *saturated* water vapour is negative. This is the case with some other vapours; in the case of ether it is positive.

The relation between h and c and the values of c_p, the specific heat at constant pressure may be found as follows:

Vapour: $h = c_p'' + l_p \, dp/dT = c_p'' - T(\partial v''/\partial T)_p \, . \, dp/dT$ from (47), (31b) and (29);

Liquid: $c = c_p' - T(\partial v'/\partial T)_p \, . dp/dT$.

For the liquid, c is approximately equal to c_p', since $(\partial v'/\partial T)_p$ is small, except when the critical state is approached.[2]

The specific heat of saturated vapour is negative when the heat evolved on compression (vapour always saturated) is greater than that absorbed in raising the temperature of the whole system through 1°.

From (195) and (79):

$$c_p'' - c_p' = \frac{dL_e}{dT} - \frac{L_e}{T} + \frac{L_e}{v'' - v'}\left(\frac{\partial v''}{\partial T} - \frac{\partial v'}{\partial T}\right)_p \quad . \quad . \quad (196)$$

Equation (195) was deduced, simultaneously, by Rankine[3] and Clausius[4]; (196) is due to Planck.[5] Since L_e always decreases with rise of temperature,

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[1] South Kensington Conferences, 1876; "Scientific Papers," Cambridge, 1890, V[illegible]II., p. 498.

[2] Cf. Porter, *P. M.*, 1920, **40**, 211.

[3] *Trans. R. Soc. Edin.*, 1850, **20**, 147.

[4] *A. P.*, 1850, **79**, 368; *P. M.*, 1851, **2**, 14.

[5] "Vorlesungen über Thermodynamik," 3rd ed., 1911, p. 152; cf. Mathias, *C. R.*, 1894, **119**, 404, 849; Amagat, *ibid.*, 1900, **130**, 1443; "Notes sur la Physique," 65 ff. On specific heat of saturated vapours, etc., see Callendar,

h will always increase (algebraically); if negative it passes through zero at a certain temperature and then becomes positive.

In the case of water at 100° C., with the data given above and the additional data: $v'' = 1674$ c.c.; $v' = 1{\cdot}0$ c.c.; $\partial v''/\partial T = 4{\cdot}813$; $\partial v'/\partial T = 0{\cdot}001$, we find $c''_p = 0{\cdot}50$, whilst Regnault found, at a temperature just over 100° C. $c''_p = 0{\cdot}48$.

The same equation may be applied to the *fusion of ice:* c_p'' (water) $= 1{\cdot}01$; c_p' (ice)[1] $= 0{\cdot}50$; $T = 273$; $v'' = 1{\cdot}0$; $v' = 1{\cdot}09$; $L_f = 80$; $\partial v''/\partial T = -0{\cdot}00006$; $\partial v'/\partial T = 0{\cdot}0001$ $\therefore$ $dL_f/dT = 0{\cdot}66$. Thus, if the melting point of ice is reduced 1° by pressure, the latent heat of fusion decreases by 0·66 cal.

The Critical Point.[2]—From (79) and (174c): $\mathrm{dp_c/dT = (s_g - s_l)/(v_g - v_l)}$ $\therefore$ at the *critical point:* $\mathrm{dp_e/dT = (ds/dv)_{Tc} = (dp/dT)_{Tc}}$ from (185a). Since $\partial\mathrm{p}/\partial\mathrm{T}$ is always finite, $\mathrm{dp_e/dT}$ is finite. From (29) and the result (99) that $(\partial\mathrm{v}/\partial\mathrm{p})_{\mathrm{Tc}} \longrightarrow -\infty$, it follows that $(\partial\mathrm{v}/\partial\mathrm{T})_{\mathrm{Tc}} \longrightarrow +\infty$.

It is a fact of experience that, in a complex of liquid and vapour, $\mathrm{dp_e/dv_l} > 0$ and $\mathrm{dp_e/dv_g} < 0$ (Fig. 17, § 46), but at the critical point they coincide and each is zero. Now (from II.*a*, § 18, by division by dv):

$$\mathrm{dT/dv_l} = (\partial\mathrm{T}/\partial\mathrm{v_l})_\mathrm{p} + (\partial\mathrm{T}/\partial\mathrm{p})_\mathrm{v} \cdot \mathrm{dp_e/dv_l}$$

and similarly for $\mathrm{dT/dv_g}$. Hence, at the critical point $\mathrm{dT/dv_l = dT/dv_g} = 0$. Also, since, near the critical point, $\mathrm{dv_l/dT} > 0$ and $\mathrm{dv_g/dT} < 0$, at the critical point $\mathrm{dv_l/dT} \longrightarrow +\infty$ and $\mathrm{dv_g/dT} \longrightarrow -\infty$.

From (79) and the properties $\mathrm{v_l = v_g}$; $\mathrm{dp_e/dT}$ and T finite, at the critical point, it follows that then $\mathrm{L_e} = 0$.

$$\text{But} \qquad \mathrm{L_e = u_g - u_l + p_e(v_g - v_l)}$$

$$\therefore \quad \mathrm{dL_e/dT = du_g/dT - du_l/dT + p_e(dv_g/dT - dv_l/dT) + L_e/T.}$$

$$\text{But } \mathrm{du_l/dT} = (\partial\mathrm{u_l}/\partial\mathrm{T})_\mathrm{v} + (\partial\mathrm{u_l}/\partial\mathrm{v_l})_\mathrm{T} \cdot \mathrm{dv_l/dT}$$

$$= \mathrm{c_{vl}} + (\partial\mathrm{u_l}/\partial\mathrm{v_l})_\mathrm{T} \cdot \mathrm{dv_l/dT}$$

$\therefore$ $\mathrm{dL_e/dT = c_{vg} - c_{vl}} + [\mathrm{p_e} + (\partial\mathrm{u}/\partial\mathrm{v})_\mathrm{T}]\,\mathrm{(dv_g/dT - dv_l/dT)}$ at the critical point, since $\mathrm{L_e} = 0$ and $(\partial\mathrm{u_l}/\partial\mathrm{v_l})_\mathrm{T} = (\partial\mathrm{u_g}/\partial\mathrm{v_g})_\mathrm{T}$ (phases identical). Substituting $\mathrm{dv_g/dT}$ and $\mathrm{dv_l/dT}$ from above, we find $\mathrm{dL_e/dT} \longrightarrow -\infty$.

It is assumed that $\mathrm{c_v}$ is always finite and positive,[3] hence from (48) $\mathrm{c_p} \longrightarrow +\infty$ just below the critical point.

EXAMPLES X

1. Find the difference in entropy of 1 gm. of water at 0° and at 100° at 1 atm. pressure, the specific heat of water being assumed constantly = 1.

2. Find the difference in entropy of 1 gm. of water and 1 gm. of ice at 0° and 1 atm. if the latent heat of fusion is 80 cal. per gm.

3. Find the difference in entropy of 1 mol of water at 10° and 1 atm. and 1 mol of steam at 100° and 0·1 atm., taking the latent heat of evaporation as 538·7 gm. cal. per gm. and assuming steam an ideal gas.

P. R. S., 1900, **67**, 266; J. P. Dalton, *P. M.*, 1907, **13**, 536; Dieterici, *A. P.*, 1903, **12**, 154; Bruhat and Delaygue, *C. R.*, 1922, **174**, 937; Mathias, Crommelin and Onnes, *C. R.*, 1922, **174**, 1395; Babcock, *Proc. Amer. Acad. Arts and Sci.*, 1920, **55**, 327. Energy and entropy of a mixture of liquid and saturated vapour, see Partington, "Text-book of Thermodynamics," 1913, § 91.

[1] Dickinson and Osborne (*J. Washington Acad. Sci.*, 1915, **5**, 338) give c (ice) $= 0{\cdot}5057 + 0{\cdot}001863\,\theta$; $L_f = 79{\cdot}76$ (20° gm. cal.).

[2] Cf. P. Sorel, *J. P. C.*, 1902, **6**, 474.

[3] Cf. Duhem, "Mécanique chimique," I., 164.

4. Calculate the increase in entropy when 1 mol of bromine is converted from the solid state at − 7·32° (m. pt.) to vapour at the boiling point 61·55°, given specific heat of liquid = 0·107 ; latent heat of fusion = 16·185 gm. cal. per gm., of evaporation, 43·69.

5. According to Rudberg the latent heat of fusion of lead is 5·86 cals. per gm. If the melting point of lead is 327° C., calculate the entropy change when 4 mols of lead are fused.

6. Show that $(\partial T/\partial p)_v \cdot (\partial s/\partial v)_p = (\partial T/\partial v)_p \cdot (\partial s/\partial p)_v + 1$.

7. Show that $(\partial p/\partial s)_T \cdot (\partial v/\partial T)_s = (\partial p/\partial T)_s \cdot (\partial v/\partial s)_T - 1$.

8. Prove the relations :

$$(\partial p/\partial u)_v = (\partial T/\partial u)_v \cdot (\partial s/\partial v)_u - (\partial T/\partial v)_u \cdot (\partial s/\partial u)_v$$

$$(\partial s/\partial u)_T = (\partial v/\partial u)_T \cdot (\partial p/\partial T)_u - (\partial v/\partial T)_u \cdot (\partial p/\partial u)_T$$

and interpret their meaning in words.

9. The diminution of energy per unit increase of volume at constant entropy (adiabatic changes) is measured by the pressure.

10. The increase of energy per unit increase of entropy at constant volume is measured by the absolute temperature.

11. Show that for a small change of state of an ideal gas :

$$Q = c_v v dp/(c_p - c_v) + c_p p dv/(c_p - c_v)$$

12. The values of $\frac{1}{2}C_p$ for 1 mol of KCl are as follows :

T° K. .	22·8	30·1	39·0	52·8	70	86	137
½Cp. .	0·58	0·98	1·83	2·80	3·79	4·36	5·25

Find the entropy and free energy changes when 1 mol of KCl is heated from 25° K. to 100° K. Assuming $U = 0$ and $S = 0$ at 0° K., find the energy and entropy of 1 mol of KCl at 50° K. (Use graphical methods.)

13. The volume of 1 gm. of liquid Hg at the B.P. is 0·07846 c.c. Assuming Hg vapour to be a perfect gas, calculate the free energy change when 1 mol Hg is evaporated at its boiling point (375° C.).

14. Calculate the difference in free energy of 1 mol of liquid Cl_2 and 1 mol of gaseous Cl_2, the pressure in each case being 1 atm. and the temperature the B.P. of Cl_2 (= − 33·6° C.). Assuming Cl_2 to be a perfect gas and given that the latent heat of evaporation of Cl_2 is 61·9 kg. cals. per mol, find the difference of intrinsic energy between the two states.

15. The boiling point of ethyl alcohol is 78·4° C. under 760 mm. pressure. The coefficient of cubical expansion is 0·001101 (mean) and the density at 17° C. is 0·9988. Assume alcohol vapour to be a perfect gas and calculate the change in free energy when 1 mol alcohol is evaporated at the boiling point.

16. Find the change in free energy in cal. when 1 mol of water is evaporated at 100° C. and 1 atm. Assume $v_g = 1674$ c.c., $v_l = 1$ c.c. Find also the change in thermodynamic potential.

17. Show that $c_v = -T(\partial^2F/\partial T^2)$; $c_p - c_v = T(\partial^2F/\partial T\partial v)^2/(\partial^2F/\partial v^2)$.

18. Show that $\epsilon_\theta = v(\partial^2F/\partial v^2)$; $l_v = -T(\partial^2F/\partial T\partial v)$.

19. Show that $c_p = -T(\partial^2Z/\partial T^2)$; $l_p = -T(\partial^2Z/\partial T\partial p)$.

20. From the condition that du for a homogeneous body is a perfect differential deduce that

$$(ds/dT)_v = c_v/T$$

and that

$$(ds/dv)_T = (1/T)[p + (du/dv)_T].$$

Thence show that $(ds/dv)_T = (dp/dT)_v$.

The rise in B.P. per unit increase of pressure for quinoline is ·058824 at the B.P. Calculate the increase of entropy per unit increase of volume at this temperature.

21. Show from the relations in the above example that for a homogeneous substance, the sum of the increase in c_p per unit increase of pressure at constant temperature and of the product of temperature into the rate of change of dv/dT with temperature at constant pressure is zero.

22. If the specific heat of liquid Cl_2 is 0·223 find the entropy difference between 1 gm. liquid Cl_2 at − 50° C. and 1 gm. at − 40° C. (pressure = 2 atm.).

23. Lewis and Randall have deduced the following equation expressing the dependence of the thermodynamic potential change on the temperature of the reaction $NO + \frac{1}{2}O_2 = NO_2$ (gas) ; $\Delta Z = -14{,}170 + 2{\cdot}75T \ln T - 0{\cdot}0028T^2 + 0{\cdot}0_631T^3 + 2{\cdot}73T$. This is based on the results of Bodenstein and Katayama (1909). Given that the thermodynamic potential change for the reaction $\frac{1}{2}N_2 + \frac{1}{2}O_2 = NO$ (gas) is 20,850 cals., calculate ΔZ for the reaction $\frac{1}{2}N_2 + O_2 = NO_2$ at 25° C.

24. The entropy per gm. atom of graphite is 1·3 cals./1° C. at 25° C. and of diamond 0·6 cals./1°C. According to Roth and Wallach (1913) the heat of combustion of diamond exceeds that of graphite by 180 cals. Calculate the value of ΔZ at 25° C. for the conversion of graphite into carbon.

25. Show that an isothermal system is in equilibrium when its free energy is a minimum. Thence show that a perfect gas at a constant temperature will always fill completely its containing vessel.

26. The specific volume v_1 of saturated ammonia vapour is given by the equation (Babcock) :

$$v_1 = 338{\cdot}990 - 172{\cdot}7327\theta + 46{\cdot}2976\theta^2 - 7{\cdot}6262\theta^3 + 0{\cdot}73653\theta^4 - 0{\cdot}035417\theta^5 + 0{\cdot}000527 8\theta^6$$

where θ is the temperature in °C. Similarly if v_2 is the specific volume of saturated liquid :

$$v_2 = 1{\cdot}49380 + 0{\cdot}079723\tau - 0{\cdot}014021\tau^2 + 0{\cdot}0074209\tau^3 - 0{\cdot}00132917\tau^4 + 0{\cdot}0001075\tau^5$$

where $\tau = (\theta + 20)/20$.

By means of equation (196) calculate the specific heat of saturated liquid ammonia at 40° C., given that the specific heat of saturated vapour at this temperature is − 3·578.

[The heat of vaporisation of NH_3 is given by the equation :

$\log_{10} L = 1{\cdot}56817 - 2{\cdot}822 \times 10^{-5}(406{\cdot}0-T) + 0{\cdot}43387 \log_{10}(406{\cdot}0-T)$.]

27. Using the data given in the above question (26) calculate the specific heat of saturated ammonia vapour at 90° C., given that the specific heat of the saturated liquid at that temperature is 5·986.

28. According to Martini (1880) c_v for Cl_2 at 0° C. is 0·083. What is the entropy increase per unit rise of temperature at 0° C. ? (See Ex. 20).

29. Find the dissipation of energy when 100 c.c. of oxygen are mixed with 400 c.c. of nitrogen at 17° C. and 1 atm. pressure. Find the concentration and the partial pressure of oxygen in the mixture. How much entropy is generated in the process ?

30. The latent heat of vaporisation, L_e, of ether is given by the equation :

$$\log L_e = 3{\cdot}165779 - 1{\cdot}423343 \log(T_c-T) + 0{\cdot}3939319[\log T_c-T)]^2$$

(Taylor and Smith, 1922) where T_c = critical temperature of ether vapour. The specific heat of liquid ether, according to Regnault, is related to the temperature by the equation : $c = 0{\cdot}529 + 0{\cdot}000592\theta$, where θ is in °C. Calculate the specific heat of saturated ether vapour at − 10° C. if T_c = 193·8° C.

31. Find the tangent of the angle between the vapour pressure curves (in mm.) of ice and water at 0°, given the latent heats of fusion and evaporation. Density of ice = 0·9168 at 0° C. : L_f = 79·77 ; specific vol. water vapour at 0° C. = 209·905 lit.

32. The latent heat of evaporation of ether at 20° is 87·54 ; at 40°, 82·83 ;

and at 100°, 68·42 (grm. cal.). Find the value at 0°. The specific heat of liquid ether is 0·56 ; find c_p for ether vapour at the boiling point, 34·6°, given that $\frac{dp}{dT}$ for ether at the boiling point is 26·9 mm./1° ; the density of liquid ether at that temperature is 0·695 ; the coefficient of cubical expansion of the liquid is $1 \cdot 63 \times 10^{-3}$ and that of the vapour is $\frac{1}{273}$; whilst the specific volume of saturated ether vapour at 34·6° = 320 c.c. Compare the calculated with the observed value of 0·428.

CHAPTER XI

The Equation of Maximum Work

74. The Equation of Maximum Work.—A system is *normally defined* when its state is specified in terms of temperature T and n other variables, $x_1, x_2 \ldots x_n$, chosen in such a way that no work is done when the temperature changes provided the x's remain constant. Thus, in the case of a gas, the *normal* variables are v and T, and not p and T. The system is then said to have $n + 1$ *degrees of freedom.*

Consider a reversible change in which a system passes isothermally from the state :

$$T, (x_1)_0, (x_2)_0, \ldots (x_n)_0$$

to the state :

$$T, x_1, x_2, \ldots x_n.$$

From (180) : $\Delta F = \Delta U - T\Delta S$

$$\therefore \quad (\partial\Delta F/\partial T)_{\Delta x} = (\partial\Delta U/\partial T)_{\Delta x} - T(\partial\Delta S/\partial T)_{\Delta x} - \Delta S$$

in which the subscript shows that $\partial\Delta F$, etc., are the changes in ΔF, etc., when the above (finite) process is carried out at $(T + dT)$ instead of at T, *i.e.*, $(x_1) - (x_1)_0$, etc., are constant.

From (38a) and (174b) the first two terms on the right cancel :

$$\left.\begin{aligned} \therefore \quad & (\partial\Delta F/\partial T)_{\Delta x} = -\Delta S = (\Delta F - \Delta U)/T \\ \text{or:} \quad & A_T + \Delta U = T(\partial A_T/\partial T)_{\Delta x} \end{aligned}\right\} \quad . \quad (197)$$

where $\Delta F = -A_T$ and $\Delta U = Q$.

This equation, which may be called the *equation of maximum work*, was first deduced by Horstmann in 1872[1]; it was used in a special case by Gibbs,[2] and generally by Helmholtz in 1882.[3]

An alternative deduction is the following :

The Second Law of Thermodynamics states that the fraction of a given quantity of heat Q_1, absorbed from the source at the absolute temperature T_1, which is convertible into work in a reversible *cycle*, with a refrigerator at the temperature T_2, is:

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[1] *A.*, 1872, 8th suppl. Bd., p. 112 ; Ostwald's *Klassiker*, No. 137, p. 14.

[2] "Scientific Papers," I., 411, 271; cf. Lord Kelvin, *P. R. S.*, 1858, 9, 255; Wegscheider, *Z. p. C.*, 1920, 94, 739.

[3] *B. B.*, 1882, p. 22 ; Ostwald's *Klassiker*, No. 124, p. 27.

$$Q_1 - Q_2 = Q_1(T_1 - T_2)/T_1.$$

Let $T_1 - T_2$ be very small $= dT$, and let $T_1 = T$.

The available part of $Q_1 = Q$ is then very small. Let it be denoted by (dA). Then:

$$(dA) = QdT/T.$$

But if ΔU is the (finite) increase of intrinsic energy of the system when the heat Q is absorbed, and A_T is the (finite) maximum work done when the *process* involving the absorption of Q takes place, then: $Q = \Delta U + A_T$. Thus:

$$(dA) = (A_T + \Delta U)dT/T$$

$$\therefore \quad A_T + \Delta U = T\,(dA)/dT.$$

The only difficulty now is the interpretation of $(dA)/dT$. For this purpose we consider a particular case, viz., the *expansion of an ideal gas.*

Let 1 mol of gas be taken, and let the expansion range always between the fixed volume limits V_1 and V_2, *i.e.*, between the vertical lines in Fig. 27.

When the expansion occurs reversibly at the temperature T the work done is represented by the area $v_1aa'v_2$, and is given by:

$$A_T = RT \ln (V_2/V_1).$$

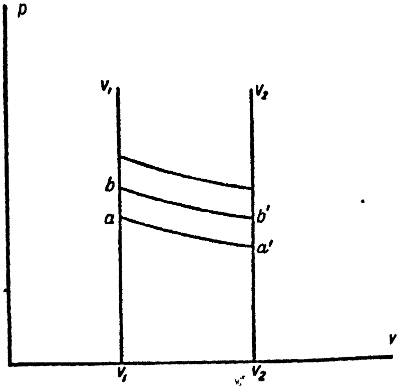

FIG. 27.

Now, suppose the expansion from V_1 to V_2 reversed at the temperature $T + dT$. The work spent is now represented by the area $b'bv_1v_2$:

$$A_T + dA_T = R(T + dT) \ln (V_2/V_1).$$

A cycle has been completed and the *excess* of work required to reverse at $T + dT$ a change which has occurred at T is:

$$(dA_T) = RdT \ln (V_2/V_1).$$

We may also consider (dA_T) as the excess of work obtained when a process is carried out reversibly with a fixed range of normal variables at a temperature $T + dT$ as compared with the work obtained when the process is carried out, *between the same range of normal variables*, at a temperature T. Thus:

$$(d\mathrm{A_T})/d\mathrm{T} = (d\mathrm{A_T}/d\mathrm{T})_{\Delta x}.$$ In this example $\Delta x = \mathrm{V}_2 - \mathrm{V}_1$.

In the integration of (197) we write it in the form:

$$\frac{d}{d\mathrm{T}}\left(\frac{\mathrm{A}}{\mathrm{T}}\right) = \frac{1}{\mathrm{T}}\cdot\frac{d\mathrm{A}}{d\mathrm{T}} - \frac{\mathrm{A}}{\mathrm{T}^2} = \frac{\mathrm{Q}_v}{\mathrm{T}^2}$$

$$\therefore \qquad \mathrm{A/T} = \int \mathrm{Q}_v/\mathrm{T}^2 \,.\, d\mathrm{T}$$

or

$$- \Delta\mathrm{F/T} = \int \mathrm{Q}_v/\mathrm{T}^2 \,.\, d\mathrm{T}$$

where $-\Delta\mathrm{F}$ is the value of $\mathrm{F}_0 - \mathrm{F}$ at the temperature T.

If Q_v is known as a function of temperature, in the manner explained in § 22, the value of $\Delta\mathrm{F}$ may be calculated, but will include an unknown constant of integration. If $\Delta\mathrm{F}$ is known for *one* temperature, this constant may be eliminated.[1]

Thus, if the true specific heats are functions of temperature of the form:

$$\mathrm{C}_v = a + \beta\mathrm{T} + \gamma\mathrm{T}^2 + \ .\ ., \text{ then}$$

$$\mathrm{Q}_v = \mathrm{Q}_0 + \Sigma a \,.\, \mathrm{T} + 1/2 \,.\, \Sigma\beta\mathrm{T}^2 + 1/3 \,.\, \Sigma\gamma\mathrm{T}^3 + \ .\ .$$

$$\therefore\ \Delta\mathrm{F} = \mathrm{Q}_0 - \Sigma a \,.\, \mathrm{T}\ln\mathrm{T} - 1/2 \,.\, \Sigma\beta\mathrm{T}^2 - 1/6 \,.\, \Sigma\gamma\mathrm{T}^3 - \ .\ . + \mathrm{IT}$$

where I is the integration constant, which may be eliminated if $\Delta\mathrm{F}$ is known at any one temperature. If the system is in equilibrium, at constant volume, at this temperature, $\Delta\mathrm{F} = 0$.

If the system is defined in terms of the $n + 1$ *normal* variables (*generalised co-ordinates*) $x_1, x_2, x_3, \ldots x_n$, and T, instead of the *two* independent variables considered in § 70, we have, for a small change of all the independent variables:

$$\delta\mathrm{A} = \mathrm{X}_1 dx_1 + \mathrm{X}_2 dx_2 + \ .\ . + \mathrm{X}_n dx_n = \Sigma\mathrm{X}_1 dx_1 \quad . \quad . \quad . \quad (198)$$

since there is no term involving T. X is called a *generalised force*, or *intensity*.

Also $\delta\mathrm{Q} = d\mathrm{U} + \delta\mathrm{A} = (\partial\mathrm{U}/\partial\mathrm{T})_x\, d\mathrm{T} + \Sigma(\partial\mathrm{U}/\partial x_1)_\mathrm{T}\, dx_1 + \Sigma\mathrm{X}_1 dx_1$
$= \mathrm{T}(\partial\mathrm{S}/\partial\mathrm{T})_x\, d\mathrm{T} + \mathrm{T}\Sigma(\partial\mathrm{S}/\partial x_1)_\mathrm{T} dx_1.$

We can now proceed as in § 70 and find:

$$[\partial(\mathrm{U} - \mathrm{TS})/\partial\mathrm{T}]_x \equiv (\partial\mathrm{F}/\partial\mathrm{T})_x = -\mathrm{S} \quad . \quad . \quad . \quad . \quad (199)$$

$$[\partial(\mathrm{U} - \mathrm{TS})/\partial x_1]_\mathrm{T} \equiv (\partial\mathrm{F}/\partial x_1)_\mathrm{T} = -\mathrm{X}_1 \quad . \quad . \quad . \quad (200)$$

$$\mathrm{U} = \mathrm{F} - \mathrm{T}(\partial\mathrm{F}/\partial\mathrm{T})_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (201)$$

If the independent variables are $\mathrm{X}_1, \mathrm{X}_2 \ldots \mathrm{X}_n$, T:

$$\delta\mathrm{Q} = \mathrm{T}\{(\partial\mathrm{S}/\partial\mathrm{T})_\mathrm{X} d\mathrm{T} + \Sigma(\partial\mathrm{S}/\partial\mathrm{X}_1)_\mathrm{T} d\mathrm{X}_1\}$$

$$d\mathrm{U} = (\partial\mathrm{U}/\partial\mathrm{T})_\mathrm{X} d\mathrm{T} + \Sigma(\partial\mathrm{U}/\partial\mathrm{X}_1)_\mathrm{T} d\mathrm{X}_1$$

$$\delta\mathrm{A} = \Sigma\mathrm{X}_1\{(\partial x_1/\partial\mathrm{X}_1)_\mathrm{T} d\mathrm{X}_1 + (\partial x_1/\partial\mathrm{T})_\mathrm{X} d\mathrm{T}\}$$

which now involves dT.

Let $\mathrm{Z} = \mathrm{U} - \mathrm{TS} + \Sigma\mathrm{X}_1 x_1$, then, as before:

$$(\partial\mathrm{Z}/\partial\mathrm{T})_\mathrm{X} = -\mathrm{S}\,;\ (\partial\mathrm{Z}/\partial\mathrm{X}_1)_\mathrm{T} = x_1 \quad . \quad . \quad . \quad . \quad . \quad (202)$$

$$\mathrm{U} = \mathrm{Z} - \mathrm{T}(\partial\mathrm{Z}/\partial\mathrm{T})_\mathrm{X} - \Sigma\mathrm{X}_1 x_1 = \mathrm{Z} - \mathrm{T}(\partial\mathrm{Z}/\partial\mathrm{T})_\mathrm{X} - \Sigma\mathrm{X}_1(\partial\mathrm{Z}/\partial\mathrm{X}_1)_\mathrm{T} \ . \quad (203)$$

---

[1] Helmholtz, *B. B.*, 1882, p. 22; Oswald's *Klassiker*, No. 124, p. 28.

An equation corresponding with (197) may be deduced for the case where *the external pressure is constant.*[1] We have:

$$Z = U - TS + pV \quad \therefore \quad \text{from (184):}$$
$$U = Z - T(\partial Z/\partial T)_p - pV.$$

From (35): $U + pV = H$

$$\therefore \qquad H = Z - T\,(\partial Z/\partial T)_p \quad . \; . \; . \; . \; . \quad (204)$$

The heat absorbed in a reversible isothermal change at constant pressure is then:

$$Q_p = H_2 - H_1 = (Z_2 - Z_1) - T\,.\,\partial(Z_2 - Z_1)/\partial T$$

or
$$\boldsymbol{\Delta H = \Delta Z - T(\partial \Delta Z/\partial T)_p} \quad . \; . \; . \quad \mathbf{(205)}$$

But $-\Delta Z = A_T'$, the maximum work minus the external work $p\Delta V$ (§ 71):

$$\therefore \qquad \boldsymbol{Q_p + A_T' = T(\partial A_T'/\partial T)_p} \quad . \; . \; . \quad \mathbf{(206)}$$

The integration of (205—206) is carried out in the same way as that of (197). If

$$C_p = \alpha' + \beta' T + \gamma' T^2 + \, . \, .$$
$$Q_p = \Delta H = Q_0 + \Sigma\alpha' \,.\, T + 1/2\,.\,\Sigma\beta' T^2 + 1/3\,.\,\Sigma\gamma' T^3 + \, . \, .$$
$$\therefore \quad \Delta Z = Q_0 - \Sigma\alpha' T \ln T - 1/2\,.\,\Sigma\beta' T^2 - 1/6\,.\,\Sigma\gamma' T^3 - \, . \, . + I'T$$

from which the integration constant I' may be eliminated if a value of ΔZ, or of $A_T' = -\Delta Z$, is known at one temperature. If the system is in equilibrium, under a constant pressure, then at this temperature $\Delta Z = 0$.

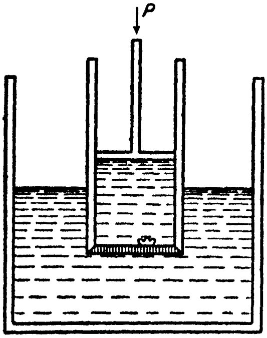

FIG. 28.

75. Effect of Temperature on Solubility.—Let a quantity of the *saturated* solution be contained in a cylinder fitted with a semi-permeable base in contact with pure solvent (Fig. 28). The system is in equilibrium at a temperature T with the solution under an osmotic pressure P.

By raising the piston allow sufficient solvent to enter reversibly to dissolve an additional mol of solid. The pressure remains constant and equal to P. The work done is $A_T = P.\Delta V$.

Let the heat absorbed be λ', the *reversible heat of solution in a saturated solution.*

---

[1] Gibbs, "Scientific Papers," I., 271; Nernst, "Grundlagen des neuen Wärmesatzes," p. 171 ff.

The equation of maximum work then gives ($\Delta x = \Delta V = $ const.):

$$T.\Delta V.\ dP/dT = \Delta U + A_T = \lambda' \quad . \quad . \quad . \quad . \quad (207)$$

But, on the assumption of an ideal solution (even though saturated):

$$P = cRT, \text{ where } c = \text{concentration} = 1/\Delta V, \text{ hence:}$$

$$\Delta V.\frac{dP}{dT} = \frac{1}{c}.\frac{d(cRT)}{dT} = RT\frac{d \ln c}{dT} + R$$

$$A_T = P\Delta V = RT$$

$$\therefore \quad \lambda' - RT = \Delta U = \lambda = RT^2 d \ln c/dT \quad . \quad . \quad . \quad [208]$$

λ = calorimetric heat of solution in a saturated solution, which may be determined from the heat of solution at any given concentration, when the relation of the heat of solution to concentration is known (§ 95).

Equation [208] may be integrated on the assumption that λ is independent of temperature, which may be true over a small range of temperature:

$$\ln c = \int(\lambda/RT^2)dT = -\lambda/RT + const. \quad . \quad . \quad [209]$$

$$\mathbf{\ln\frac{c_2}{c_1} = \frac{\lambda}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \quad . \quad . \quad . \quad . \quad \mathbf{[210]}$$

from which λ may be calculated.

The use of [209] as a solubility equation may be improved by assuming $\lambda = \lambda_0 + aT$, as in the analogous case of evaporation (86); we then find:

$$\log c = A + B/T + C \log T \quad . \quad . \quad . \quad . \quad [211]$$

analogous to the vapour pressure equation (87a); this holds over fairly wide ranges of temperature.

Equation [210] is due to Le Chatelier (1885)[1] and van't Hoff (1885)[2]; equation [211] was deduced by the author and R. T. Hardman (1911).[3] The form $\lambda_0 + aT$ was justified by data of the specific heats of solutions.

The solubilities of succinic acid at 0° C. and 8·5° C. are 2·88 and 4·22 gm./100 gm. H_2O; $\ln c_2/c_1 = 2{\cdot}3026 \log (4{\cdot}22/2{\cdot}88)$; $R = 1{\cdot}987$

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[1] Le Chatelier, *C. R.*, 1885, **100**, 441.

[2] Van't Hoff, *A. N.*, 1886, **20**, 239; *P. M.*, 1888, **26**, 81; Rudolphi, *Z. p. C.*, 1895, **17**, 277. Numerical data, Winkelmann, "Physik," III., 819 ff.; cf. Schröder, *Z. p. C.*, 1893, **11**, 449; Washburn and Read, *N. A.*, 1915, **1**, 191; Roozeboom, *Z. p. C.*, 1889, **4**, 49; Deventer and van de Stadt, *ibid.*, 1892, **9**, 43; Mortimer, *J. A. C. S.*, 1922, **44**, 1416.

[3] R. T. Hardman and J. R. Partington, *C. S.*, 1911, **99**, 1769.

cal./1° $\therefore \lambda = 1{\cdot}987 \times (\log 4{\cdot}22 - \log 2{\cdot}28) \times 2{\cdot}3026/(1/273 - 1/281{\cdot}5) = 6{\cdot}85$ kg. cal. (obs. 6·70).

If the solute changes its molecular state on dilution we may put:

$$P = icRT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [212]$$

where $i = f(c, T)$, van't Hoff's factor (§ 57), depends on T and the dilution:

$$\therefore \quad \lambda = \lambda' - iRT$$

$$dP/dT = R(iT \,.\, dc/dT + ic + Tc \,.\, di/dT)$$

$$\therefore \quad \lambda = iRT^2 \,.\, d\ln c/dT + RT^2 \,.\, di/dT \quad . \quad . \quad . \quad [213]$$

When the range of temperature is small, [213] may be integrated on the assumption that i is constant ($di/dT = 0$):

$$\ln c = -\lambda/iRT + const. \quad . \quad . \quad . \quad . \quad . \quad [214]$$

In the case of the *ionisation of a binary electrolyte* (§ 91):

$$i = 1 + a \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (215)$$

and

$$a^2c = K(1 - a) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [216]$$

where a is the degree of ionisation, and K is a constant for a particular temperature (*Ostwald's dilution law*). Thus [213] may be written:

$$\lambda/RT^2 = (1 + a) \,.\, d\ln c/dT + da/dT \quad . \quad . \quad . \quad [213a]$$

Differentiate [216] with respect to T, divide the left side by a^2c and the right by $(1 - a)K$, and rearrange:

$$\frac{da}{dT} = \frac{a(1-a)}{2-a} \cdot \frac{d\ln K}{dT} - \frac{a(1-a)}{2-a} \cdot \frac{d\ln c}{dT}.$$

Substitute in [213a]:

$$\therefore \quad \frac{\lambda}{RT^2} = \frac{2}{2-a} \cdot \frac{d\ln c}{dT} + \frac{a(1-a)}{2-a} \cdot \frac{d\ln K}{dT} \quad . \quad . \quad [217]$$

an equation deduced by Noyes and Sammet (1903).[1] In the case of *o*-nitrobenzoic acid, λ calcd. by [217] = 6,480 gm. cal.; λ obs. = 6,025 gm. cal.

Consider the *isomeric change* $A \rightleftharpoons B$ in solution. Then $K = c_A/c_B$ (§ 90). The vapour space will also contain the substances (possibly in very small amounts), and here $K' = c_A'/c_B'$. By § 52 $c/c' = s'$, the *solubility* of the vapour. If p is the vapour pressure of the *solid*, and s its solubility in the liquid, $s = s'p$. Hence: $c_A/c_B = (s_A/s_B) \,.\, K' \,.\, (p_B/p_A) = G.s_A/s_B$, where $G = K'p_B/p_A$ is independent of the nature of the solvent. Thus, two isomeric

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[1] *Z. p. C.*, 1903, **43**, 513; cf. Cohen and Bruins, *Z. p. C.*, 1919, **93**, 43; Steinwehr, *Z. p. C.*, 1920, **94**, 6; Le Chatelier, "Sur les équilibres chimiques," Paris, 1888, 138.

(tautomeric) substances are in equilibrium in any solvent when their concentrations are in the ratio of their solubilities. This relation is due to van't Hoff[1]; it has been confirmed by Dimroth[2] and Vixseboxse.[3] The latter found with benzoyl camphor the ratios *enol/ketone:* in toluene 82/18; in alcohol 61/39; in acetone 52/48, corresponding with the relative solubilities in these solvents. With optical isomers $c_A = c_B$, and $s_A = s_B$ in *all* solvents.

A method of determining the transition temperature of two forms of a substance from their solubilities at two temperatures has been given.[4]

76. The Gibbs-Helmholtz Equation for Reversible Cells.—An important application of the equation of maximum work is the determination of the effect of temperature on the electromotive force of a reversible cell.

A *reversible cell* is one in which an opposing E.M.F. infinitesimally greater than the E.M.F. of the cell reverses the direction of the current through the cell and all the material changes taking place in the latter. A reversible cell with an equal opposing E.M.F. forms a system in true equilibrium.

The first calculation of the E.M.F. of a cell from thermal data was made independently by Helmholtz[5] and Lord Kelvin,[6] and assumed that the electrical work was equal to the heat of reaction (evolved) in the cell:

$$A_T' = -Q \equiv \mathcal{Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad (218)$$

In the calculation we take 1 kgm. cal. = $4{\cdot}184 \times 10^{10}$ ergs; 1 *joule* = volt × coulomb = 10^7 ergs; hence 1 kgm. cal. = $4{\cdot}184 \times 10^3$ joules.

The number of coulombs transported per chemical equivalent of change in the cell is given by Faraday's law, and is found experimentally[7] to be:

$$F = 96{,}500 \text{ coulombs } (O = 16).$$

The value of F depends ultimately on the atomic weight of silver, since the ampère is defined in terms of the weight of silver deposited in one second under specified conditions from a solution of a silver salt; F, therefore, depends on the unit of atomic weight adopted. The above value refers to O = 16·00.

If E is the E.M.F. of the cell in volts, the work of decomposition of 1 gm. *equivalent* of electrolyte will be:

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[1] "Lectures on Theoretical Chemistry," Eng. tr., vol. 1, p. 221.

[2] *A.*, 1910, **377**, 127 ff.

[3] *Rec. trav. chim.*, 1921, **40**, 1.

[4] J. Meyer, *Z. E.*, 1911, **17**, 976: the equation T_0 (transit.) = $T_1T_2 \ln c_1'c_2''/(T_1 \ln c_1'/c_1'' - T_2 \ln c_2'/c_2'')$, where c', c'' refer to the two forms, is easily found from [210] and the relation $\lambda'' - \lambda'$ = heat of transition.

[5] "Uber die Erhaltung der Kraft," Berlin, 1847, p. 48.

[6] Thomson, *P. M.*, 1851, **2**, 429.

[7] Bates and Vinal, *J. A. C. S.*, 1914, **36**, 916. This is probably more accurate than the usual value. 96.540.

$EF = 96{,}500E$ joules, and if Thomson's (Kelvin's) rule is true:

$$E = Q \text{ kgm. cal.} \times 4{\cdot}184/96{\cdot}5 = Q \text{ kgm. cal.}/23{\cdot}06 \quad . \quad . \quad (218a)$$

In the case of the Daniell cell, which was used by Lord Kelvin in testing his equation, the heat of reaction may be calculated as follows:

$$\underset{198\cdot8 \text{ kgm. cal.}}{CuSO_4Aq + Zn} = \underset{248\cdot7 \text{ kgm. cal.}}{ZnSO_4Aq} + Cu + Q$$

$\therefore$ $Q = 248{\cdot}7 - 198{\cdot}8 = 49{\cdot}9$ kgm. cal. The heat of reaction per gm. equivalent is thus $49{\cdot}9/2 = 25$ kgm. cal. The calculated voltage is $25/23{\cdot}1 = 1{\cdot}08$. The observed voltage is 1·09, in good agreement.

In a similar way the rule may be applied to calculate *decomposition voltages*, on the assumption that the minimum E.M.F. which must be applied to electrolyse a solution is equal to the maximum E.M.F. developed in a cell when the reverse reaction takes place. In this case irreversible changes, giving rise to over-voltage, are neglected.

(i.) Electrolysis of fused salt (Acker process):

$$NaCl = Na + Cl - 96{\cdot}6 \text{ kgm. cal.}$$

hence $E = 96{\cdot}6/23 = 4{\cdot}2$ volt. (Obs. = 6·75 volt.)

(ii.) Electrolysis with the sodium dissolved in mercury (Castner-Kellner cell). The heat of solution of Na in mercury is 19·1 kgm. cal., hence $E = (96{\cdot}6 - 19{\cdot}1)/23 = 3{\cdot}37$ volt. (Obs. 4·3 volt.)

(iii.) Electrolysis of brine (Billiter cell):

$$\underset{96\cdot6}{NaCl} + \underset{69}{H_2O} = \underset{112\cdot5}{NaOH} + H + Cl$$

hence $E = (96{\cdot}6 + 69 - 112{\cdot}5)/23 = 2{\cdot}31$ volt. (Obs. 3·1 volt.)

The agreement is moderate, but the actual voltages are always one or two volts above the calculated.

In the case of the cell:

$$Ag/KCl \text{ sol. satd. with } AgCl/Cl_2 \text{ gas}$$

E is 1·167 volt $\therefore$ $A'_T = 2 \times 1{\cdot}167 \times 23$ kgm. cal. $= 2 \times 26{\cdot}8$ kgm. cal. The heat of reaction: $2Ag + Cl_2 = 2AgCl$ is $2 \times 29{\cdot}4$ kgm. cal. Only a fraction $26{\cdot}8/29{\cdot}4 = 0{\cdot}91$ of the heat of reaction (diminution of intrinsic energy) is here available as electrical work (diminution of available energy).

In some cases A' and Q may even differ in sign. The cell making use of the endothermic reaction $HgCl + KOH = \frac{1}{2}Hg_2O + KCl + \frac{1}{2}H_2O$ may furnish current, *i.e.*, A'_T is positive, whilst Q is negative.[1]

The Thomson rule is analogous to the Berthelot-Thomsen rule, that the heat of reaction is a measure of the affinity of a reaction, which is considered in § 82, and the error in the two rules is made clear by (206):

$$A_T' = Q_p + T(\partial A_T'/\partial T)_p.$$

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[1] Bugarszky, *Z. an. C.*, 1897, **14**, 145; Gerke, *J. A. C. S.*, 1922, **44**, 1684.

The term $T(\partial A_T'/\partial T)_p$ represents the *latent heat* absorbed when the cell operates reversibly, and the rule is not true unless $\partial A_T'/\partial T = 0$. In the present case *the E.M.F. must be independent of temperature,* which is rarely the case, but is approximately true in the case of the Daniell cell. The true relation between E.M.F. and heat of reaction may be derived from this equation.

$$A_T' = EF \text{ per gm. equiv.} \quad . \quad . \quad . \quad . \quad (219)$$

Q_p = calorimetric heat of reaction *per gm. equiv.*

Thus:
$$\mathbf{E}F = Q_p + \mathbf{T}F\,.\,d\mathbf{E}/d\mathbf{T} \quad . \quad . \quad . \quad . \quad \mathbf{(220)}$$

Let $q = Q_p/F$ and $\lambda = EF - Q_p$. q is the heat of reaction (evolved) per *electrochemical* equivalent, and λ is called the *latent heat* of the cell (*absorbed*) per chemical equivalent: λ is a measure of the deviation from the Thomson-Helmholtz rule. Then:

$$\lambda = TF\,.\,dE/dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (220a)$$

and
$$E = q + T\,.\,dE/dT \quad . \quad . \quad . \quad . \quad . \quad . \quad (221)$$

This equation, deduced by Helmholtz,[1] has been confirmed by several experimenters, notably by Jahn.[2] It may be used to determine the *heat of reaction* of the process occurring in the cell, and the latter compared with that determined directly; or, if the heat of reaction is assumed, the value of dE/dT may be calculated, and compared with that found experimentally. In both cases the agreement is satisfactory.

An equation identical in principle with Helmholtz's was deduced in 1878 by Gibbs,[3] who also showed that if the cell exhibits a *transition point* ($E = 0$ for $T = T_0$), then:

$$E = q(1 - T/T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (222)$$

The correctness of this is most readily seen by differentiating with respect to T:

$$dE/dT = -\,q/T_0$$

$\therefore$ from (222) we recover (221). Equation (222) is particularly noteworthy, since it enables a free energy (EF) to be calculated from purely thermal data (q, T_0, T). Conversely, the equation may be used to determine transition temperatures.[4]

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[1] *B. B.*, 1882, p. 22; Ostwald's *Klassiker*, No. 124, p. 21; cf. Brôdy, *A. P.*, 1914, **44**, 591.

[2] *A. P.*, 1886, **28**, 21, 491; 1893, **50**, 189; cf. Lehfeldt, "Electrochemistry," 1908, pp. 177 ff.

[3] "Scientific Papers," I., 338 ff., where the effects of pressure and gravity are also considered; cf. *ibid.*, pp. 406 ff. for (222).

[4] Cohen, *Z. p. C.*, 1894, **14**, 53; Cohen and Bredig, *ibid.*, 535.

Equation (219) is often the most convenient method of calculating affinity, and (220) heat of reaction.

EXAMPLES XI.

1. Calculate the change of thermodynamic potential for the cell Hg/Hg_2Cl_2 + 0·01N.KCl in $N.KNO_3/N.KNO_3$/0·01 N.KOH + Hg_2O in $N.KNO_3/Hg$, the E.M.F. of which is 0·1636 at 18·5° C.

2. Find the change in intrinsic energy of the cell Hg/Hg_2Cl_2, 0·01.N.KCl, $N.KNO_3/N.KNO_3/N.KNO_3$, 0·01 N.KI, Hg_2I_2(yellow)/Hg, the E.M.F. of which is 0·3086 volt at 18·5° C. (Bugarszky), dE/dT being $-$ 0·00027. Calculate also the latent heat of this cell at 18·5° C.

3. The heat of the reaction $Hg_2Cl_2 + 2KBr = Hg_2Br_2 + 2KCl$ is 4010 gm. cals. If the E.M.F. of the cell Hg/Hg_2Cl_2, 0·01 N.KCl in $N.KNO_3/N.KNO_3$/0·01 N.KBr + Hg_2Br_2 in $N.KNO_3/Hg$ is 0·2149 volt at 43·3° C., show that the temperature coefficient of the cell is $-$ 0·000144 volt/° C.

4. Calculate the decrease of thermodynamic potential for the cell $Cu/N.CuSO_4/N.ZnSO_4/Zn$, the E.M.F. of which is 1·1 volt at 18° C. Give the answer in calories.

5. If $E = 0\ 0579$ volt at 25° C. for the cell Ag/0·01 $N.AgNO_3$/sat. NH_4NO_3/ 0·001 $N.AgNO_3/Ag$, find the thermodynamic potential decrease when the cell is working, expressing the answer in both calories and joules.

6. The solubility of AgCl at 18° C. is $1{\cdot}17 \times 10^{-5}$ mol per litre ; that at 25° C. is $1{\cdot}6 \times 10^{-5}$ mol. Calculate the mean heat of solution between these temperatures. Thomsen found the value 15,800 cals., experimentally.

7. The electrode potential of Mg in $MgSO_4$ solution (1 mol/lit.) is 1·55 volt, whilst that of Pb in $Pb(NO_3)_2$ solution of a similar strength is 0·13 volt. (Temp. = 25° C. ; E for H_2 electrode = 0.) Calculate the thermodynamic potential change for a cell composed of these two electrodes.

8. The transition point between monoclinic and rhombic sulphur is 95° C. when $p = 1$ atm. The atomic heats of these modifications are: S (rhombic), $c_p = 4{\cdot}12 + 0{\cdot}0047T$ and S (monoclinic), $c_p = 3{\cdot}62 + 0{\cdot}0072T$. The heat of transition of monoclinic to rhombic sulphur is 77·0 cals. per gm. atom (evolved) at 0° C. Show that at 25° C. the rhombic form of S is the more stable. Show also that the heat of transition at 0° K. is 120 cals. per gm. atom.

9. In the case of a potassium perchlorate solution at 20° C., for which $\ln c = 0{\cdot}04175T +$ const., the value of i, van't Hoff's factor, = 1·795, this number decreasing 0·00295 per degree rise in temperature. Show that the heat of solution of $KClO_4$ in a saturated solution is 12,270 cals., approximately, the observed value being 12,130 cals.

10. Test equation [211] for solutions of anthracene in benzene, for which $A = -7{\cdot}1236$, $B = 1466{\cdot}751$ and $C = 0{\cdot}7960$ (c is in gms. per 100 gms. solvent) :

Temp. °C.	c (obs.)	Temp. °C.	c (obs.)
10	0·975	50	3·75
20	1·43	60	5·14
30	2·03	70	7·00
40	2·78		

11. The solubility of sucrose in water is :

179·2 gms. per 100 gms. water at 0° C.
219·5 „ „ „ 30° C.
and 320·5 „ „ „ 70° C.

Find the solubility at 50° C. and at 10° C. (use [211]).

12. The solubility of succinic acid in 100 gms. water is 2·35 gms. at 0° C. and 6·76 gms. at 24·8° C. Assuming these solutions to be undissociated, find λ, the heat of solution of one mol of the acid, assuming it independent of the temperature.

13. At 34·12° C. the solubility of AgCl in water is $2{\cdot}74 \times 10^{-4}$ per cent. and at 4·68° C. it is $6{\cdot}6 \times 10^{-5}$ per cent. (*i.e.*, gms. per 100 gms. solution). Assuming AgCl to be completely dissociated in each of these solutions, calculate the heat of solution of 1 mol (assumed independent of temperature).

14. The ratio between the number of molecules of dissolved salt (n) to the total number of molecules present ($N + n$) in a saturated solution of silver acetate is given by the equation :

$$c = \frac{n}{N + n} = 0{\cdot}0_3 80292 + 0{\cdot}0_4 13647t + 0{\cdot}0_6 1099t^2$$

where t is the temperature in °C. Show that the calorimetric heat of solution of this salt in a saturated solution is, at 25° C., 2·775 gm. cals. ; at 30° C. 2·806 gm. cals. ; at 35° C., 2·832 gm. cals.

15. The solubility of silver isovalerate (Molec. wt. = 208·43) is given by the equation

$$s = 0{\cdot}1774 + 0{\cdot}003349\ (t - 0{\cdot}2) + 0{\cdot}0_5 6528\ (t - 0{\cdot}2)^2,$$

s being the solubility in gms. per 100 gms. water. Show that the heat of solution per mol of this salt is 2·34 cals. at 25° C. and 2·368 cals. at 35° C.

16. The heat of transition of grey tin to white tin at 0° C. is 532 cals. per gm. atom (absorbed). The difference of the specific heats of these two varieties of tin is given by : $c_p\ (\text{white}) - c_p\ (\text{grey}) = 0{\cdot}49 + 3{\cdot}25 \times 10^{-8} (300 - \mathrm{T})^3$, which holds for all temperatures between − 193° C. and 19° C. Deduce an equation expressing the heat of transition as a function of temperature ; find the value of this heat at 80° K. and 200° K.

Find also an expression for the affinity of the transition, given that the transition point (p = 1 atm.) is 19° C.

CHAPTER XII

Ideal Gas Mixtures

77. Entropy of an Ideal Gas.—The increase of entropy on isothermal expansion at a temperature T of 1 mol of an ideal gas from volume V_1 to volume V_2 is (see § 36):

$$(1/\mathrm{T}) \,.\int\delta\mathrm{Q} = (1/\mathrm{T}) \,.\, \mathrm{RT} \,.\, \ln(V_2/V_1) = \mathrm{R}\ln(V_2/V_1) \,. \quad [223]$$

Let *unit mass* of gas pass reversibly from the state v, T to the state $v + dv$, $\mathrm{T} + d\mathrm{T}$:

$$du = \mathrm{T}ds - pdv \quad \therefore \quad ds = (du + pdv)/\mathrm{T}.$$

But $du = c_v d\mathrm{T}$, and $p = \mathrm{RT}/\mathrm{M}v$, where M = molecular wt.

$$\therefore \quad ds = c_v \,.\, d\mathrm{T}/\mathrm{T} + (\mathrm{R}/\mathrm{M}) \,.\, dv/v$$

$$\therefore \quad s = \int(c_v/\mathrm{T})d\mathrm{T} + (\mathrm{R}/\mathrm{M})\ln v + s_0 \,. \quad . \quad . \quad [224]$$

where the integration constant s_0 = entropy in an arbitrary standard state, v_0, T_0. The entropy s depends only on the *actual state* of the gas and not on how it is brought into that state.

If $c_v = const.$, $\quad s = c_v \ln \mathrm{T} + (\mathrm{R}/\mathrm{M})\ln v + s_0 \quad . \quad . \quad . \quad [224a]$

78. Free Energy of an Ideal Gas.—$\mathrm{F} = \mathrm{U} - \mathrm{TS}$, or for unit mass: $f = u - \mathrm{T}s$. Now:

$$u = \int c_v d\mathrm{T} + u_0 \quad \therefore \text{ from } [224]$$

$$\begin{aligned} f &= u_0 - \mathrm{T}s_0 + \int c_v d\mathrm{T} - \mathrm{T}\int(c_v/\mathrm{T})d\mathrm{T} - (\mathrm{RT}/\mathrm{M})\ln v \\ &= g'(\mathrm{T}) - (\mathrm{RT}/\mathrm{M})\ln v \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [225] \end{aligned}$$

where $\quad g'(\mathrm{T}) = u_0 - \mathrm{T}s_0 + \int c_v d\mathrm{T} - \mathrm{T}\int(c_v/\mathrm{T})d\mathrm{T} \quad . \quad . \quad [226]$

79. Thermodynamic Potential of an Ideal Gas.

$$z = f + pv = f + \mathrm{RT}/\mathrm{M} \text{ for unit mass,}$$

$$\therefore \quad z = g'(\mathrm{T}) - (\mathrm{RT}/\mathrm{M})(\ln v - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad [227]$$

The *values for* 1 *mol of gas* are easily found. Let $\mathrm{M}u = U$; $\mathrm{M}c_v = \mathrm{C}_v$; $\mathrm{M}s = S$; $\mathrm{M}v = V$; $\mathrm{M}f = F$; $\mathrm{M}z = Z$;

$$\begin{aligned} S &= S_0 + \int(\mathrm{C}_v/\mathrm{T})d\mathrm{T} + \mathrm{R}\ln V - \mathrm{R}\ln \mathrm{M} \\ &= S_0' + \int(\mathrm{C}_v/\mathrm{T})d\mathrm{T} + \mathrm{R}\ln V \quad . \quad . \quad . \quad . \quad . \quad [228] \end{aligned}$$

where $S_0' = S_0 - \mathrm{R}\ln\mathrm{M}$.

$$F = U_0 - TS_0' + \int C_v dT - T\int (C_v/T)dT - RT \ln V \quad . \quad . \quad . \quad [229]$$

$$Z = U_0 - TS_0' + \int C_v dT - T\int (C_v/T)dT - RT(\ln V - 1) \quad . \quad [230]$$

Thus if $g(T) = Mg'(T) + RT \ln M$:

$$F = g(T) - RT \ln V \quad . \quad . \quad . \quad . \quad . \quad . \quad [231]$$

$$Z = g(T) - RT(\ln V - 1) \quad . \quad . \quad . \quad [232]$$

We note that F and Z contain an arbitrary linear function of temperature, $U_0 - TS_0' = a + \beta T$, say.

80. **Ideal Gas Mixture.**—The mixing of gases was studied by Dalton (1801), who found that:

(1) If two or more gases are put together either by stratifying or by connecting the containing vessels, they mix uniformly by diffusion.

(2) If different gases mix by diffusion at the same temperature and pressure, then, provided no chemical change takes place:

(*a*) the volume of the mixture is the sum of the volumes of its constituents;

(*b*) the temperature remains unchanged throughout the process (this was regarded as indicating absence of chemical action by Scheele in 1777).

We define an *ideal gas mixture* as one which has a free energy equal to the sum of the free energies of the separate gases, each at the same temperature and occupying the same volume as the mixture. We shall show that this gives the known properties of mixtures of gases.

Let there be given initially the volumes $V_1, V_2, \ldots$ of the gases $G_1, G_2, \ldots$, contained in separate vessels, all at the temperature T. Let $n_1, n_2, \ldots$ be the numbers of mols of the gases.

Now let the vessels be put in communication so that all the gases mix. Let the temperature of the mixture be kept at T. The total volume occupied by the mixture is $V = V_1 + V_2 + \ldots = \Sigma V_1$.

The *free energy of the first (unmixed) gas* is, by [231]:

$$F_1 = - n_1 RT \ln (V_1/n_1) + n_1 g_1(T)$$

$\therefore$ the *total free energy of the unmixed gases* is:

$$F_0 = - RT\Sigma n_1 \ln (V_1/n_1) + \Sigma n_1 g_1(T) \quad . \quad . \quad . \quad [233]$$

The *total free energy of the mixed gases* is, by definition:

$$F = - RT\Sigma n_1 \ln (V/n_1) + \Sigma n_1 g_1(T) \quad . \quad . \quad . \quad . \quad [234]$$

$\therefore$ the ***diminution of free energy on mixing*** is:

$$F_0 - F = RT\Sigma n_1 \ln (V/V_1) \quad . \quad . \quad . \quad . \quad . \quad [235]$$

$\therefore$ mixing of gases by diffusion is a spontaneous process (cf. § 63). The value of the diminution of free energy on mixing is the same as that previously found (§ 64) without the definition of the ideal gas mixture.

The equation of maximum work (197) gives

$$U_0 - U = (F_0 - F) - T\partial(F_0 - F)/\partial T.$$

Differentiate [235] with respect to T, and substitute in this

$$\therefore \qquad U_0 - U = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [236]$$

i.e., no heat is evolved or absorbed on mixing ideal gases without performance of external work. This result may be regarded as an extension of Joule's Law (§ 33).

If p = total pressure of the mixture, then from (183)

$$-\partial F/\partial V = p.$$

Differentiate [234] with respect to V (T const.) and substitute in (183):

$$\therefore \quad p = \Sigma n_1 RT/V = \Sigma p_1 \quad . \quad . \quad . \quad . \quad . \quad [237]$$

where $p_1 = n_1RT/V$ = pressure exerted by the first gas when confined alone in the whole volume of the mixture. Equation [237] is, therefore, the expression of Dalton's *Law of partial pressures.*

The definition of an ideal gas mixture adopted is therefore consistent with the known properties of mixtures of ideal gases.[1]

EXAMPLES XII.

1. Show that the increase in entropy on mixing 250 c.c. N_2 with 500 c.c. O_2 at a pressure of 800 mm. is 0·044 cal./1° C.

Show also that if the mixing is carried out at 27° C. the maximum work is 13·33 cals.

2. Calculate the entropy decrease due to the isothermal compression of 25 litres of chlorine to 15 litres at 35° C.

Explain carefully why it is that this entropy decrease is identical with the decrease of entropy due to compressing, say, 5 litres of CO_2 to 3 litres at the same temperature. (Assume the perfect gas laws in each case.)

3. Show that for a gas which obeys van der Waals' equation exactly, $S = C_v \log T + R \log (V - b) + S_0$, S_0 being an arbitrary constant.

4. Calculate the entropy change due to mixing 70 litres H_2 at 157° C. and under a pressure of 20 atm. with 60 litres of N_2 at the same temperature and pressure, both gases being assumed ideal.

5. Thirty litres of NO diffuse into 30 litres of SO_2 under a (constant) total

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[1] In the case of non-ideal gases, Leduc (*A. C. P.*, 1898, [vii.], **15**, 106) assumes that the *volume* occupied by a mixture of gases is equal to the sum of the *volumes* which each gas would occupy at the pressure and temperature of the mixture. This is found experimentally to be much nearer the truth than Dalton's law of partial pressures; it holds approximately even up to 200 atm. pressure, with mixtures of hydrogen and nitrogen (cf. "Physical and Chemical Data of Nitrogen Compounds," H.M. Stationery Office, 1918, p. 6; Amagat, "Notes sur la physique," p. 82; Kuenen, "Verdampfung und Verflüssigung von Gemischen," pp. 99–106 (bibliography).

pressure of 2 atms., and at a temperature of 0° C. Assuming no volume change takes place on mixing, calculate the total entropy increase.

6. Find the changes of F and Z when 1 mol of a gas is (*a*) heated at a constant volume of 1 litre, and (*b*) at a constant pressure of 1 atm., from 0° to 100° C.

7. Find the changes of F and Z when 1 mol of gas is heated from 0° to 100° C. at a constant volume of 1 litre and then expanded at 100° to 10 litres.

8. Find the changes of F and Z when 1 mol of gas is expanded from 1 litre to 10 litres at 0° C. and then heated at constant volume to 100° C. Compare with Ex. 7. What does the result show ?

9. If a gas obeys Boyle's law the diminution of potential on isothermal expansion is equal to the diminution of free energy.

10. Show that the free energy and potential of a gas for which the true specific heat is a linear function of temperature $c_v = a + b\mathrm{T}$ are:

$$\mathrm{F} = \mathrm{U}_0 - \mathrm{TS}_0 - a\mathrm{T}\ln\mathrm{T} - b\mathrm{T}^2 - (\mathrm{R}/\mathrm{M})\,\mathrm{T}\ln v + (a + 2b)\mathrm{T}$$
$$\mathrm{Z} = \mathrm{U}_0 - \mathrm{TS}_0 - a\mathrm{T}\ln\mathrm{T} - b\mathrm{T}^2 - (\mathrm{R}/\mathrm{M})\mathrm{T}(\ln v - 1) + (a + 2b)\mathrm{T}.$$

In the case of oxygen, if $c_v = 0{\cdot}148 + 0{\cdot}000076t$° C., find the changes in F and Z for an expansion from $v = 1$ to $v = 10$ litres at 0° C., stating the units in which the results are expressed.

CHAPTER XIII

Chemical Equilibrium in Gases

81. Maximum Work of a Chemical Reaction between Gases.—Chemical reactions may be *reversible*, and then *states of equilibrium* may be established. If the smallest increase or decrease in the concentration of any one constituent leads to a small chemical change, the reaction taking place in such a direction as to diminish or increase the concentration of that constituent, respectively, the state is one of *true equilibrium*. It is readily shown from this definition that the true equilibrium state is the same whether we start with the substances on the left or those on the right of the reaction equation.

The state of equilibrium is defined by T, v (or p), and *the chemical composition*. We thus require more variables than in the case of a fluid of fixed composition. Since the state of equilibrium is independent of the total amount of the system, the composition variables will be the relative amounts of the constituents, *i.e.*, the *concentrations*.

The concentrations may be expressed in various ways. The *volumetric molar concentration*, denoted by c, or C, gives the number of mols, n, per litre. In general we shall use c for the *equilibrium concentrations*, and C for the initial or other arbitrary *free concentrations*. If $V =$ total volume, $c_1 = n_1/V$.

We have as a general expression for the *maximum work* of a reaction:

$$A_T = F_0 - F = -\Delta F.$$

E.g., $2H_2 + O_2 \rightarrow 2H_2O$; $A_T = [2F_{H_2} + F_{O_2}] - 2F_{H_2O}$,

where the values of F refer to 1 mol of free unmixed gas at the temperature of the reaction and at given arbitrary concentrations, C_{H_2}, etc.

Gases	H_2	O_2	H_2O
Free concentrations . .	C_{H_2}	C_{O_2}	C_{H_2O}
Equilibrium concentrations .	c_{H_2}	c_{O_2}	c_{H_2O}

Take 2 mols of H_2 at concentration C_{H_2} and 1 mol of O_2 at concentration C_{O_2}, and suppose the two gases converted isothermally and reversibly into 2 mols of H_2O at concentration C_{H_2O}. What work is done ?

$F_0 = 2F_{H_2} + F_{O_2} = 2RT \ln C_{H_2} + RT \ln C_{O_2} + 2g(T)_{H_2} + g(T)_{O_2}$ for the unmixed gases, from [233] with the substitution $V_1/n_1 = 1/C_1$; and :

$$F = 2F_{H_2O} = 2RT \ln C_{H_2O} + 2g(T)_{H_2O}.$$

Thus :

$$A_T = F_0 - F = RT \ln (C^2_{H_2}C_{O_2}/C^2_{H_2O}) + f(T) \quad . \quad . \quad . \quad (X)$$

where $f(T) = 2g(T)_{H_2} + g(T)_{O_2} - 2g(T)_{H_2O}$

is a function of temperature which must now be determined. For this purpose we suppose that c_{H_2}, c_{O_2}, and c_{H_2O} are the concentrations in a mixture of the three gases which is *in equilibrium.*

Then, if we allow the change $2H_2 + O_2 \rightarrow 2H_2O$ to take place in such a way that the initial concentrations of hydrogen and oxygen are c_{H_2} and c_{O_2}, and the concentration of steam formed is c_{H_2O}, the only work done will be the external work :

$$A_T = F_0 - F = \text{external work.}$$

For, let the change take place by adding 2 mols of H_2 at the concentration c_{H_2}, and 1 mol of O_2 at the concentration c_{O_2}, to the equilibrium mixture, and at the same time removing 2 mols of H_2O (gaseous) at the concentration c_{H_2O}. The gas mixture in equilibrium is supposed to be contained in an impervious box (the "equilibrium box"), and the gases are added to or removed from

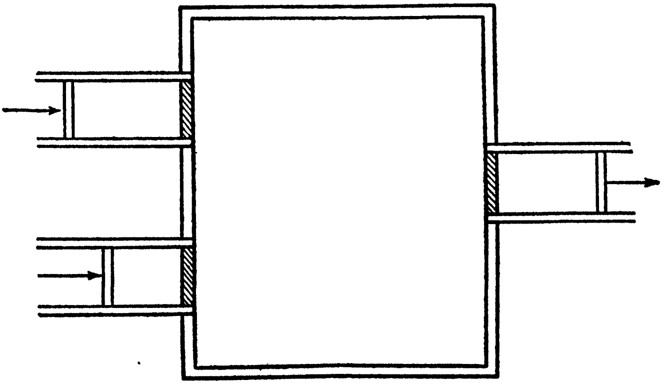

FIG. 29.

the box by cylinders fitted with impervious pistons and communicating with the box through selectively permeable septa, as shown in Fig. 29. In this the left-hand upper cylinder contains the hydrogen, the left-hand lower cylinder the oxygen, and the right-hand cylinder the steam. If the steam is removed as fast as it is formed the composition and amount of the equilibrium mixture in the box remains constant.

The work done is 2RT − 2RT − RT = − RT, or, generally Σn_1RT. Thus, by substituting in (X) we find:

$$A_T = -RT = RT\ln(c^2_{H_2}c_{O_2}/c^2_{H_2O}) + f(T)$$

hence:

$$f(T) = -RT - RT\ln(c^2_{H_2}c_{O_2}/c^2_{H_2O}).$$

But $c^2_{H_2O}/c^2_{H_2}c_{O_2} = K$, the *equilibrium constant*,[1] hence:

$$\begin{aligned} A_T &= RT\ln K + RT\ln(C^2_{H_2}C_{O_2}/C^2_{H_2O}) - RT \\ &= RT\ln K - RT\ln(C^2_{H_2O}/C^2_{H_2}C_{O_2}) - RT. \end{aligned}$$

This result is easily generalised. Let the chemical reaction be:

$$n_1G_1 + n_2G_2 + \ldots = n_1'G_1' + n_2'G_2' + \ldots$$

and let $n_1' + n_2' + \ldots - (n_1 + n_2 + \ldots) = \Sigma n_1$ *i.e.*, the *increase* in the number of mols in the reaction, and similarly let:

$$\Sigma n_1 \ln C_1 = n_1' \ln C_1' + n_2' \ln C_2' \ldots - (n_1 \ln C_1 + n_2 \ln C_2 + \ldots)$$

where logarithms of concentrations of *products* of reaction are taken as *positive*, and those of the initial reacting substances taken as negative. Also, let:

$$\begin{aligned} \ln K &= n_1' \ln c_1' + n_2' \ln c_2' + \ldots - (n_1 \ln c_1 + n_2 \ln c_2 + \ldots) \\ &= \Sigma n_1 \ln c_1. \end{aligned}$$

Then $$\mathbf{A_T = RT\ln K - RT\Sigma n_1 \ln C_1 + RT\Sigma n_1} \quad [238]$$

This most important equation is sometimes called the equation of the *Reaction Isotherm.*

A_T depends only on the initial and final states of the system, and on T, *i.e.*, for a fixed temperature it depends only on the values of the C's. Hence, at a fixed temperature K is a constant. This is the *Law of Mass Action*, which is here deduced from thermodynamic considerations. This deduction is due to van't Hoff (1886),[2] although the deduction from thermodynamics had been effected by Horstmann in 1873,[3] and by Willard Gibbs in 1876.[4] The deduction from the kinetic theory is due to Guldberg and

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[1] See Partington, "Text-book of Inorganic Chemistry," 1921, ch. xx.

[2] Ostwald's *Klassiker*, No. 110.

[3] Ostwald's *Klassiker*, No. 137.

[4] "Scientific Papers," vol. 1 p. 172.

Waage in 1864.[1] K is a constant only when T is constant; it is, in general, a function of temperature.

82. Affinity of a Reaction.—Julius Thomsen, in 1853, recognised that the *affinity* between reacting substances is connected in some way with the *energy changes* attending their reaction. The affinities of halogens for hydrogen is clearly in the ascending order: iodine, bromine, chlorine, fluorine, since any one halogen is displaced from its hydracid by any other succeeding it in this series. The heats of formation of the hydracids also increase in the same series:

HF 38·5 kgm. cal. HBr 8·44 kgm. cal. (from liquid Br_2)
HCl 22 kgm. cal. HI – 6·04 kgm. cal. (from solid I_2)

Thomsen therefore proposed to take the *heat of reaction*, or the diminution of intrinsic energy (see § 21) as a measure of the affinity. In the decomposition of an exothermic compound an expenditure of energy is required, and according to Thomsen only those substances could bring about decomposition which themselves develop more heat than is absorbed in the decomposition. Metals such as zinc, iron, and magnesium, the oxides of which are formed with the evolution of more heat than is developed in the formation of water vapour from the same amount of oxygen, are able to decompose steam, but if the heat of oxidation of the metal is less than the heat of formation of steam, the metal (*e.g.*, silver) is unable to decompose the latter.

A similar principle was advanced by Berthelot in 1865,[2] and was called the *Law of Maximum Work.* It assumed that only those reactions take place spontaneously which are attended by an evolution of heat.

Numerous exceptions to the law were found. In particular:

(1) It implies that a reaction can proceed in one direction only, viz., that in which heat is evolved, and reversible reactions should be impossible. But any correct measure of affinity must clearly involve the equilibrium constant.

(2) Every endothermic reaction, of which there are very many, is an exception to the law.

Although Berthelot tried to overcome the objections by further ingenious assumptions,[3] it must be recognised that the Law of

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[1] Ostwald's *Klassiker*, No. 104.

[2] See, especially, "Thermochimie," I., 1897, pp. 7 ff.; "Essai de Mécanique chimique," 1879, vol. 1, p. 28; vol. 2, pp. 417 ff.

[3] In the (endothermic) formation of acetylene in the arc, for instance, it was assumed that the carbon was first of all turned into gas (with absorption of heat) and then combined with hydrogen (with evolution of heat).

Maximum Work in its original form is incorrect. At the time it was advanced it was, however, quite in harmony with the progress of physical science. Lord Kelvin (1851)[1] and Helmholtz (1847)[2] (see § 76) had previously made use of an identical assumption in calculating the electromotive forces of cells. The first correct statement of the relations involved was due to Gibbs in 1876, but his differential equations made no appeal to chemists. Helmholtz, in 1882 [3] (see § 74), gave a more intelligible account of the matter by pointing out that the correct measure of the affinity is the *work* which can be done by the chemical forces ("Arbeitswerth der chemischen Verwandtschaftkräfte"), *i.e.*, the diminution of *Free Energy*, or the Maximum Work, of the reaction. This is by no means the same thing as the Heat of Reaction, or the diminution of Intrinsic Energy; in some cases the two may be opposite in sign.[4] In naming the principle the law of maximum *work*, not the law of maximum *heat*, Berthelot seems to have had a prophetic intuition of the real state of affairs, but he remained faithful to his original formulation long after it had been shown, by his own numerous thermochemical measurements, to be incorrect.

Since those changes can occur spontaneously which involve dissipation of energy, the diminution of available energy in a reaction is a criterion of the manner in which the reaction will proceed, apart from precise details (cf. § 66). The principle of dissipation of energy was applied to chemical changes by Lord Rayleigh in 1875 (cf. § 64); the related entropy principle of Clausius was made use of in a similar way by Horstmann in 1873 (cf. § 41).

The correct measure of the affinity of a reaction is the diminution of Free Energy.[5] The consequences of this statement for chemistry are as yet hardly realised, but with the further progress of the science it is to be expected that empirical results will more and more give way to exact quantitative laws. The ultimate aim of theoretical chemistry is to arrive at a general method of calculating affinities from as small a number of experimental data as possible. It is not impossible that these data may ultimately be reduced to the dimensions and masses of the atoms, but the influence of passive resistances will no doubt prove a fundamental difficulty.[6]

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[1] *P. M.*, 1851, **2**, 429.
[2] Ostwald's *Klassiker*, No. 1, 1889.
[3] Ostwald's *Klassiker*, No. 124.
[4] Bugarszky, *Z. an. C.*, 1897, **14**, 145.
[5] See R. Plank, *Z. p. C.*, 1922, **100**, 372.
[6] Partington, *Chemical Age*, 1922, pp. 850, 884.

In " L'Etude de Dynamique Chimique " (Amsterdam, 1884), van't Hoff opens the chapter on Affinity (p. 177), as follows :

" In this chapter we shall deduce from what has preceded, without making use of any hypotheses whatsoever, the value of affinity, either by considering it as a force and therefore expressing it in kilograms or in atmospheres, or by indicating the work which the force can do, work which in this case will be expressed in kilogram-metres or in calories. This last manner of viewing it leads to the following simple and general conception :

" The work of affinity (A) is equal to the heat which produces the transformation (*q*) divided by the absolute temperature of the transition point (P) and multiplied by the difference between this latter temperature and T, the temperature at which the change takes place :

$$A = q\frac{P - T}{P}."$$

The value of A_T given by [238] may therefore be taken as a measure of the chemical affinity in a reaction between gases. It includes the external work, $RT\Sigma n_1$, but this is not always recoverable in measurements of the maximum work. Thus, if the affinity of the reaction $2H_2 + O_2 = 2H_2O$ is measured by the E.M.F. of the Grove's gas battery, the work done in the disappearance of the gases, 3RT, does not appear as an equivalent of electrical work. Most writers omit the external work, and take, as the measure of the affinity, A_T minus the external work, *i.e.*, A_T', or the diminution of thermodynamic potential Z (§ 71). In this case :

$$\textbf{Affinity} = Z_0 - Z = -\Delta Z = A_T' \quad . \quad . \quad . \quad . \quad (239)$$

and equation [238] must then be modified by leaving out the term $RT\Sigma n_1$:

$$\textbf{Affinity} = A_T' = RT \ln K - RT\Sigma n_1 \ln C_1 \quad . \quad . \quad [240]$$

If the reaction occurs without change of volume A_T and A_T' are identical.

If all the free concentrations are unity (1 mol per litre) :

$$A_T' = RT \ln K \quad . \quad . \quad . \quad . \quad . \quad . \quad [241]$$

It may be noted that this provides a method of determining K.

83. Alternative Deduction of the Maximum Work of a Gas Reaction.—The work done in changing the concentration of 1 mol of an ideal gas from C_1 to C_2 is (§§ 11, 36) $RT \ln (V_2/V_1) = RT \ln (C_1/C_2)$, since the concentration is inversely proportional to the volume, *i.e.*, RT ln (*initial conc./final conc.*).

Let hydrogen and oxygen gases be taken at the *free concentrations* C_{H_2} and C_{O_2}, and converted into steam at the free concentration C_{H_2O}. The operation is carried out isothermally and reversibly by means of the arrangement described in § 81, except that now the gases are taken in the exterior cylinders at the actual free concentrations, and the latter must therefore be altered by reversible compression or expansion to the *equilibrium concentrations* before the gases can be passed into the box; and the steam removed from the box at the equilibrium concentration must afterwards be brought to its free concentration by reversible expansion or compression in the cylinder. During these compressions, the selectively permeable septa are shut off, as in § 53. The total work done is readily calculated according to the scheme below, the directions of change being shown by the arrows :

Gas	Free Concentrations.		Work of Change.		Equilibrium Concentrations.
H_2 :	C_{H_2}	$\rightarrow$	$-2RT + 2RT \ln (C_{H_2}/c_{H_2})$	$\rightarrow$	c_{H_2}
O_2 :	C_{O_2}	$\rightarrow$	$-RT + RT \ln (C_{O_2}/c_{O_2})$	$\rightarrow$	c_{O_2}
H_2O :	C_{H_2O}	$\leftarrow$	$+2RT + 2RT \ln (c_{H_2O}/C_{H_2O})$	$\leftarrow$	c_{H_2O}

Thus :

$$A_T = -2RT - RT + 2RT + 2RT \ln (C_{H_2}/c_{H_2}) + RT \ln (C_{O_2}/c_{O_2}) + 2RT \ln (c_{H_2O}/C_{H_2O})$$

$$= -RT + RT \ln (c^2_{H_2O}/c^2_{H_2}c_{O_2}) - RT \ln (C^2_{H_2O}/C^2_{H_2}C_{O_2})$$

$$\therefore \quad A_T = RT \ln K - RT\Sigma n_1 \ln C_1 + RT\Sigma n_1 \quad . \quad . \quad [238]$$

in the general case, as before.[1]

84. Maximum Work in Terms of Partial Pressures.—Let p_1 be the partial pressure of a component existing at the concentration c_1 in a gas mixture. Then :

$$p_1 = n_1 RT/V = c_1 RT, \text{ or } c_1 = p_1/RT \quad . \quad . \quad [242]$$

Let the initial and final products of the reaction be under the total pressures P_1, P_2, . . . etc. Then :

$C_1 = n_1/V = P_1/RT$. Substitute for C and c in [238] :

$$A_T = RT\Sigma n_1 \ln p_1 - RT\Sigma n_1 \ln P_1 + RT\Sigma n_1 \quad . \quad . \quad [243]$$

Put $\Sigma n_1 \ln p_1 = \ln K'$, where K′ is a new equilibrium constant; then :

$$A_T = RT \ln K' - RT\Sigma n_1 \ln P_1 + RT\Sigma n_1 \quad . \quad . \quad [244]$$

$$A_T' = RT \ln K' - RT\Sigma n_1 \ln P_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad [245]$$

If the initial and final substances are under the same free pressure p, then :

$$A_T' = RT \ln K' - RT \ln p\Sigma n_1 \quad . \quad . \quad . \quad [245a]$$

$$= RT \ln K' \text{ if } p = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad [246]$$

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[1] Cf. Wegscheider, *Z. p. C.*, 1912, 79, 223, 239.

85. Application of the Reaction Isotherm.—The most important source of useful work is the combustion of carbon in the form of fuel. We shall calculate the maximum work of the reaction $C + O_2 = CO_2$ by means of [246]. For this purpose the data of Rhead and Wheeler on the equilibrium $CO_2 + C \rightleftarrows 2CO$ in presence of solid carbon at various temperatures, given in Table I.,[1] and those of Nernst and Wartenberg,[2] on the dissociation of $CO_2 : 2CO_2 \rightleftarrows 2CO + O_2$, in Table II., are used.

TABLE I. $CO_2 + C \rightleftarrows 2CO$ (1 atm.).

θ° C.	% CO_2 (vol.).	% CO (vol.).	p_{CO_2}.	p_{CO}.
850	6·23	93·77	0·0623	0·9377
900	2·22	97·78	0·0222	0·9778
950	1·32	98·68	0·0132	0·9868
1000	0·59	99·41	0·0059	0·9941
1050	0·37	99·63	0·0037	0·9963
1100	0·15	99·85	0·0015	0·9985
1200	0·06	99·94	0·0006	0·9994

TABLE II. $2CO_2 \rightleftarrows 2CO + O_2$. PERCENTAGE DISSOCIATION.

T° K.	0·1 atm.	1 atm.	10 atm.	100 atm.
1000	$0{\cdot}0_4531$	$0{\cdot}0_4247$	$0{\cdot}0_4114$	$0{\cdot}0_5531$
1500	0·104	0·0483	0·0224	0·0104
2000	4·35	2·05	0·960	0·445
2500	33·5	17·6	8·63	4·09
3000	77·1	54·8	32·2	16·9
3500	93·7	83·2	63·4	39·8

At 1000° C. we have, from the tables (1 atm.):

(i.) In the gas in equilibrium with solid carbon, 99·41% CO and 0·59% CO_2, by volume.

(ii.) CO_2 dissociated to the extent of 0·0027% (interpolated):

$$\begin{array}{cccc} 2CO_2 & \rightleftarrows \quad 2CO & + & O_2 \\ 2(1 - 0{\cdot}000027) & 2 \times 0{\cdot}000027 & & 0{\cdot}000027 \end{array}$$

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[1] *C. S.*, 1910, 97, 2178.

[2] Nernst, "Lehrbuch," 8–10 Aufl., p. 765.

$$p_{CO_2} = 1 - 0{\cdot}000027 \text{ atm.} = 1 \text{ atm. (approximately)};$$
$$p_{CO} = 0{\cdot}000027 \text{ atm.}; \; p_{O_2} = p_{CO}/2 = 0{\cdot}0000135 \text{ atm.}$$
$$K' = p^2_{CO} \times p_{O_2}/p^2_{CO_2} \quad \therefore \quad K' \times 1^2 = (0{\cdot}000027)^2 \times (0{\cdot}0000135).$$

Let $p_{O_2} = x$ atm. be the partial pressure of oxygen in equilibrium with solid carbon in the given circumstances. Then:

$$K' \times (0{\cdot}0059)^2 = (0{\cdot}9941)^2 \times x \quad \therefore \quad x = 5{\cdot}22 \times 10^{-19} \text{ atm.}$$

The reversible burning of carbon to carbon dioxide may be supposed effected in the following manner (cf. §§ 82 and 83): solid carbon is contained in the equilibrium box, oxygen at 1 atm. and 1000° C. is fed in at one side through a plate permeable only to oxygen, and carbon dioxide at 1 atm. and 1000° C. is obtained at the other side through a plate permeable to carbon dioxide only.

(1) Take 1 mol O_2 at 1 atm. and expand to pressure $x = 5{\cdot}22 \times 10^{-19}$ atm. at 1000° C. The work gained is $RT \ln (1/x)$.

(2) Admit this oxygen to the box. The work gained is $- RT$.

(3) Whilst the oxygen is being introduced, let the carbon dioxide formed be removed at its pressure in the box. The work gained is $+ RT$.

(4) Compress this carbon dioxide from 0·0059 atm. to 1 atm. The work gained is $- RT \ln (1/0{\cdot}0059) = RT \ln (0{\cdot}0059)$.

The process is completed, and the total work gained is:

$$\begin{aligned} A_T = F_0 - F &= RT \ln (1/x) - RT + RT + RT \ln (0{\cdot}0059) \\ &= RT \ln (0{\cdot}0059/5{\cdot}22 \,.\, 10^{-19}) \\ &= 4{\cdot}576 \times 1273 \times \log (0{\cdot}0059/5{\cdot}22 \,.\, 10^{-19}) \\ &= 93{,}513 \text{ cal.} \quad (R \ln y = 4{\cdot}576 \log y \text{ if R is in cal.}) \end{aligned}$$

We may now compare this with the diminution of intrinsic energy $U_0 - U$ = heat of combustion Q_v.

The heat of combustion of carbon at T = 290° K. is 94,272 cal. per gm. atom. The atomic heat of carbon from 0° to 2000° K. may be taken as $1{\cdot}1 + 0{\cdot}0048T - 0{\cdot}0_5 12T^2$, and the molecular heats of the gases at constant volume as: $C_v\ (O_2) = 4{\cdot}51 + 0{\cdot}0010T$; $C_v(CO_2) = 5{\cdot}01 + 0{\cdot}0071T - 0{\cdot}0_5 186T^2$.[1] Thence (38) gives ($T_1 = 290°$ K., $T_2 = 1273°$ K.; the above are *true* specific heats): $Q_{1273} - Q_{290} = - 646$ cal. Thus $Q_{1273} = 93{,}626$ cal. (approx.). The percentage of the intrinsic energy change which is, theoretically, convertible into useful work is $(93{,}513/93{,}626) \times 100 = 99$, which is a very large fraction. This work cannot, of course, be obtained by a heat engine, which necessarily wastes a large fraction of the heat to the refrigerator (§ 26). Thus, if the boiler operates at 600° K. and refrigerator at 300° K., the maximum work is only 50% of the heat taken from the boiler, and a certain amount of the heat of combustion is wasted before it appears in the steam. A galvanic cell burning carbon in an electrolyte would approximate to the maximum efficiency of 99%, but in spite of numerous attempts to construct such "Fuel Cells," the problem is still unsolved.[1] The master problem of chemical technology is to find such an arrangement.

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[1] Lewis and Randall, "Thermodynamics," 1923, pp. 80, 569. The values are only very approximate. For more accurate values for oxygen and CO_2, see Partington and Shilling, "Specific Heats of Gases," Benn Bros., 1924.

86. Effect of Temperature on Affinity : Reaction Isochore.—The Maximum Work (Affinity) of a chemical reaction is [238] :

$$A_T = RT \ln K - RT\Sigma n_1 \ln C_1 + RT\Sigma n_1 \text{ (Reaction Isotherm)} \quad . \quad (X).$$

Differentiate with respect to T at constant Δx, *i.e.*, constant Δv and C's in this case (§ 74) :

$$dA_T/dT = R \ln K + RTd \ln K/dT - R\Sigma n_1 \ln C_1 + R\Sigma n_1 \quad . \quad (Y).$$

Substitute A_T from (X) and dA_T/dT from (Y) in (197) :

$$\left.\begin{aligned} &\boldsymbol{d \ln K/dT = Q_v/RT^2} \\ \text{or} \quad &\boldsymbol{Q_v = RT^2 . d \ln K/dT} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad [247]$$

Equation [247], due to van't Hoff,[2] is called by Nernst the Reaction Isochore (Greek χώρα = space, or, very properly in this case, = Latin *regio*, a tract or region, viz., Δx). The general integral of [247] is :

$$\ln K = \frac{1}{R}\int \frac{Q_v}{T^2} dT + \ln K_0 \quad . \quad . \quad . \quad . \quad [248]$$

where K_0 corresponds with a standard temperature T_0. The value of K at any temperature is then given by [248], provided Q_v is known as a function of T over the range T_0 to T, which involves a knowledge of the specific heats. The latter are, therefore, of fundamental importance in chemical problems of this type. Substitute [248] in [238] :

$$A_T = T\int (Q_v/T^2) dT - RT\Sigma n_1 \ln C_1 + RT\Sigma n_1 + RT \ln K_0 \quad . \quad [249]$$

But (41) : $Q_v = Q_0 + \int (\Gamma_f - \Gamma_i) dT$. (Note $Q_{op} = Q_{ov} + \Sigma n_1 RT = Q_{ov}$ for $T = 0$.)

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[1] Cf. on the above, Weigert in Abegg's "Handbuch der anorg. Chem.," III., ii., 192 ff. ; Rideal and Evans, *F. S.*, 1922, **17**, 466 ; Haber, "Thermodynamics of Technical Gas Reactions" ; W. H. Patterson, *P. M.*, 1907, **13**, 181.

[2] "Etude de dynamique chimique," Amsterdam, 1884.

Assume $\Gamma_f - \Gamma_i = a + 2\beta T$, *i.e.*, the specific heats are linear functions of T:

$$\therefore \quad Q_v = Q_0 + aT + \beta T^2$$

$$\therefore \quad A_T = -Q_0 + aT\ln T + \beta T^2 - RT\,\Sigma n_1 \ln C_1 + RT\Sigma n_1 + RT\ln K_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad [250]$$

The simplest assumption would be to put $\Gamma_f - \Gamma_i = 0$, $\therefore$ $Q_v = Q_0 =$ const.

$$\therefore \quad \ln K = -Q_v/RT + \text{const.} \quad . \quad . \quad . \quad . \quad [251]$$

$$\ln K_2 - \ln K_1 = (Q_v/R)\,.\,(1/T_1 - 1/T_2)\,. \quad . \quad . \quad [251a]$$

$$\log K_2 - \log K_1 = (Q_v/4{\cdot}576)\,.\,(1/T_1 - 1/T_2). \quad . \quad [251b]$$

Even when the *separate* assumptions made in its deduction are not true, [251] covers most cases of equilibrium observed.[1] In the application of [247]—[251], careful attention must be paid to *sign*. We shall take the logarithms of the *products* of a reaction, *i.e.*, the values of n_1', etc., *positive*, and the heat of reaction positive when it is absorbed. Thus, in:

$$2H_2 + O_2 = 2H_2O + Q_v$$

we put, if $C_{H_2} = [H_2]$, etc. (a useful notation): $K = [H_2O]^2/[H]_2^2[O_2]$, and Q_v (evolved) is negative. With increasing T, therefore, [247] shows that K will diminish, *i.e.*, the extent of dissociation of the steam will increase. If we had written the reaction equation as:

$$2H_2O = 2H_2 + O_2 + Q_v$$

we should have had $K = [H_2]^2[O_2]/[H_2O]^2$, and Q_v is positive (absorbed), hence, with rise of temperature the dissociation will increase, as before.

The Reaction Isochore is, therefore, the quantitative expression of van't Hoff's *Law of Mobile Equilibrium:*[2] with rise of temperature in a system in equilibrium, that reaction will take place which occurs with absorption of heat. This is a special case of Le Chatelier's *Law of Reaction:* when a system in equilibrium is subjected to a constraint, whereby the equilibrium is modified, a change occurs which tends to annul the effect of the constraint. This covers the effect of pressure, temperature, change of concentration, etc., but it is important to remember that it applies only to systems in true equilibrium.[3]

A similar expression to [247] may be deduced when partial pressures are used instead of concentrations:

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[1] Scheffer, *A. A.*, 1917, **19**, 636.

[2] "Etudes de dynamique Chimique," 1884.

[3] Le Chatelier, "Les Équilibres Chimiques," 1888, p. 210; cf. Lord Rayleigh, *C. S.*, 1917, **111**, 250; Ariès, *C. R.*, 1914, **158**, 492; Raveau, *J. de P.*, 1909, **8**, 572; Berthelot, "Thermochimie," I., 13 ff.

$$\ln K' = \Sigma n_1 \ln p_1 = \Sigma n_1 \ln (c_1RT) = \Sigma n_1 \ln c_1 + \Sigma n_1 \ln RT$$
$$= \ln K + \Sigma n_1 \ln T + \Sigma n_1 \ln R$$
$$\therefore\quad d \ln K'/dT = d \ln K/dT + \Sigma n_1/T = Q_v/RT^2 + \Sigma n_1/T$$
$$= (Q_v + \Sigma n_1 RT)/RT^2 = Q_p/RT^2 \quad . \quad . \quad [252]$$

87. **Heterogeneous Reactions.**—If we consider reactions in which, besides a gaseous phase, solids or liquids *of unchanging composition* (*i.e.*, pure substances and not solid or liquid solutions) participate, the equation of the reaction isochore remains unchanged, except that the concentrations in the gas phase only are included in K or K′.[1] For, we may suppose that the condensed phases take part in the form of their vapours, the latter existing in equilibrium under pressures constant at a given temperature as long as condensed phases are present. Thus the free concentration C is always the same as the equilibrium concentration, and in calculating the maximum work the term $\ln C/c$ vanishes for all such materials. The heat of reaction must, of course, be that of the complete reaction, and in determining its change with temperature the heat capacities of all the phases, gases and condensed, must appear in $\Gamma_f - \Gamma_i$.

As an example of a heterogeneous system we may take a hydrated salt in contact with water vapour, *e.g.*, $CuSO_4, 3H_2O + 2H_2O = CuSO_4, 5H_2O + A_T'$. If p is the pressure of water vapour in equilibrium with the salts, p_0 the vapour pressure of pure water or ice at the same temperature, then $K' = 1/p^2$, and since $\Sigma n_1 = -2$:

$$A_T' = RT \ln K - RT\Sigma n_1 \ln P_1 = RT \ln 1/p^2 + RT \ln p_0^2.$$

The heat of hydration is :

$$Q_p = RT^2 . d \ln K'/dT = -2RT^2 . d \ln p/dT.$$

It is usual to refer A_T' and Q_p to 1 mol of water vapour, and in that case :

$$A_T' = RT \ln (p_0/p) \quad \text{and } Q_p = -RT^2 . d \ln p/dT . \quad [253]$$

The following values are calculated for the measurements of Schottky[2] at 0° C., all referring to 1 mol of free water in the form of ice. The values of $-Q_p = \mathcal{Q}_p$ which are to be compared with those of A_T' in considering the degree of approximation of the Thomsen-Berthelot rule (§ 82), are from the measurements of Thomsen. It will be seen that in some cases A_T' and $\mathcal{Q}_p$ are nearly equal, but that in others they differ largely. Hydrates with small dissociation pressures give large values of A_T', which is what we should expect, since the affinity between the salt and water is then large.

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[1] Cf. Williamson and Morey, *J. A. C. S.*, 1918, **40**, 49 ; Partington, "Thermodynamics," 1913, § 161.

[2] *Z. p. C.*, 1908, **64**, 415.

Reaction.	Q_p gm. cal. obsd.	A_T' gm. cal. obsd.
$CuSO_4 + H_2O$	4860	2350
$CuSO_4, 3H_2O + 2H_2O$	1190	840
$ZnSO_4, H_2O + 5H_2O$	554	480
$MnSO_4, H_2O + 4H_2O$	336	359
$FeSO_4, H_2O + H_2O$	200	275

88. Examples of the Reaction Isochore.—The equation of the Reaction Isochore is capable of a large number of applications in all branches of Physical Chemistry. Many examples will be found in the books of physical chemical problems,[1] two only will be given here to illustrate the method.

If x is the degree of *dissociation of nitrogen tetroxide :*

$$N_2O_4 \rightleftharpoons 2NO_2$$

and V is the volume of 1 mol of partially dissociated N_2O_4, then :

$x = (3{\cdot}179 - \Delta)/\Delta$, where Δ = density of the gas (air = 1), 3·179 being the (theoretical) density of N_2O_4,[2]

$$\ln K = 2 \ln c_{NO_2} - \ln c_{N_2O_4} = 2 \ln \frac{x}{V} - \ln \frac{1 - x}{V} = \ln \frac{x^2}{(1 - x)V}$$

where $V = RT(1 + x)/p = RT(1 + x)$ when $p = 1$ atm.

Thus: $$\ln K = \ln \frac{x^2}{(1 - x^2)RT}.$$

Since Q_v, the heat of dissociation, may be taken as constant over a small range of temperature :

$$\ln \frac{x_2^2}{(1 - x_2^2)RT_2} - \ln \frac{x_1^2}{(1 - x_1^2)RT_1} = \frac{Q_v}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \quad Q_v = 4{\cdot}576 \times \frac{T_1T_2}{T_2 - T_1} \log \frac{x_2^2(1 - x_1^2)T_1}{x_1^2(1 - x_2^2)T_2}.$$

The following results of Deville and Troost :

$$T_1 = 273 + 26{\cdot}7\ ; \ \Delta_1 = 2{\cdot}65 \quad \therefore \quad x_1 = 0{\cdot}1996$$

$$T_2 = 273 + 111{\cdot}3\ ; \ \Delta_2 = 1{\cdot}65 \quad \therefore \quad x_2 = 0{\cdot}9267$$

give Q_v = 12,900 gm. cal.

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[1] See Prideaux, "Problems in Physical Chemistry," 1920; Jellinek, "Physikalische Chemie der Gasreaktionen," 1913; Knox, "Physio-chemical Calculations," 1920.

[2] Partington, "Inorganic Chemistry," 1921, pp. 72, 153.

Berthelot and Ogier[1] found that in the interval 27° C. and 150° C. ($x = 1$), 92 gm. of nitrogen dioxide absorb 12,620 gm. cal. The heat capacity of the dissociating gas includes the heat required to raise the temperature from 27° C. to 150° C., which may be calculated from the molecular heat of NO_2 at high temperatures ($C_p = 16{\cdot}86$ for 92 gm.), when no heat is spent on producing dissociation. (The difference between the heat capacities of N_2O_4 and $2NO_2$ is neglected.) This gives: $16{\cdot}86\ (150 - 27) = 2074$ gm. cal.

Another part of the heat is used in doing external work owing to expansion: $RT_2(1 + x_2) - RT_1(1 + x_1) = 972{\cdot}2$ gm. cal. (§ 22).

The third part is the true heat of dissociation:

$\therefore\ Q_v(x_2 - x_1) = 12620 - (2074 + 972{\cdot}2)\ \ \therefore\ Q_v = 11{,}968$ gm. cal., as compared with 12,900 calculated.[2]

The Dissociation of Steam.

$$2H_2O \rightleftharpoons 2H_2 + O_2$$
$$K \times c_1^2 = c_2^2 \times c_3$$

where c_1 = concentration of H_2O, c_2 = concentration of H_2, c_3 = concentration of O_2, and K is the equilibrium constant.

If x is the degree of dissociation, *i.e.*, the fraction of 1 mol of steam which is broken up into hydrogen and oxygen, and if p is the pressure:

$$c_1 = \frac{p}{RT} \cdot \frac{2 - 2x}{2 + x};\ c_2 = \frac{p}{RT} \cdot \frac{2x}{2 + x};\ c_3 = \frac{p}{RT} \cdot \frac{x}{2 + x},$$

$$\therefore \qquad K = \frac{p}{RT} \cdot \frac{x^3}{(2 + x)(1 - x)^2}$$

When x is very small in comparison with 1, $K = px^3/2RT$.

Q_v for $2H_2O = 113{,}820 + 2{\cdot}65T - 4{\cdot}41.10^{-4}T^2 + 1{\cdot}252.10^{-6}T^3 - 9{\cdot}12.10^{-10}T^4 + 4{\cdot}36.10^{-17}T^6$. (Cf. § 21, Ex.)

When Q_v is inserted in $d \ln K/dT = Q_v/RT^2$, and the resulting equation integrated, it is found that:

$$\log K = -24{,}900/T + 1{\cdot}335 \log T - 0{\cdot}965.10^{-4}T + 0{\cdot}137.10^{-6}T^2 - 0{\cdot}665 . 10^{-10}T^3 + 0{\cdot}1907.10^{-17}T^5 + I$$

where I is the integration constant. The value of I can be found from *one* value of the degree of dissociation, but Siegel, by a comparison of a number of measurements, finds $I = -1{\cdot}08$. The resulting equation then gives very satisfactory calculated figures, as is seen from the following table:

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[1] *A. C. P.*, 1883, **30**, 382; cf. Nernst, *D. p. G.*, 1909, **11**, 313; Levy, *ibid.*, 330; Duhem, "Mécanique chimique," II., 312 ff.; Swart, *Z. p. C.*, 1891, **7**, 120; § 89; Einstein, *B. B.*, 1920, 380; Keutel, *Diss.*, Berlin, 1911; Selle, *Z. p. C.*, 1923, **104**, 1.

[2] Cf. van't Hoff, "Chemical Dynamics" (Lectures), tr. Lehfeldt, Vol. I., p. 144 (error in calculation). On thermal dissociation, see Gibbs, "Scientific Papers," Vol. I., p. 372, ff., where methods of calculation are explained.

DISSOCIATION OF STEAM ($p = 1$ atm.).

Method.[1]	T.	$100x$ calc.	$100x$ obs.
Gas cell . . .	290	$0·466 \times 10^{-25}$	$0·47 \times 10^{-25}$
Heated Pt wire. .	1300	0·0029	0·0027
Streaming . .	1397	0·0085	0·0078
" . .	1480	0·0186	0·0189
Heated Pt wire. .	1500	0·0221	0·0197
Streaming . .	1561	0·0369	0·034
Semi-permeable bulb.	1705	0·107	0·102
" " .	2155	1·18	1·18
" " .	2257	1·76	1·77
Explosion . .	2337	2·7	2·8
" . .	2505	4·1	4·5
" . .	2684	6·6	6·2
" . .	2731	7·4	8·2
" . .	3092	15·4	13·0

89. **The Specific Heat of a Dissociating Gas.**—If the temperature of a mixture of a gas and its dissociation products (*e.g.*, N_2O_4 and NO_2) be raised through δT at constant pressure p, the heat absorbed, $C_p\delta T$ per mol of the undissociated gas, is made up of four parts:

(i.) The heat required to warm the undissociated part through δT at constant volume $= (1 - x)C_v\delta T$, where C_v is the molecular heat of the undissociated gas (*e.g.*, N_2O_4);

(ii.) The heat required to warm the products of dissociation through δT at constant volume $= (n_1C_1 + n_2C_2 + \ldots)x\delta T$, where $C_1, C_2 \ldots$ are the molecular heats at constant volume, and $n_1, n_2, \ldots$ the numbers of mols, of the products of dissociation formed from 1 mol of undissociated gas;

(iii.) The heat equivalent of the external work $= p(\partial V/\partial T)_p\delta T$, where V = total volume (ideal gas; cf. § 19);

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[1] Cf. Partington, "Thermodynamics," 1913, pp. 353 ff.; Nernst, "Lehrbuch," 8–10 Aufl., 1921, pp. 758 ff.; Haber, "Thermodynamics of Technical Gas Reactions"; Jellinek, "Gasreaktionen."

(iv.) the heat of dissociation $= Q_v(\partial x/\partial T)_p \delta T$, Q_v being assumed constant. Thus:

$$C_p = (1 - x)C_v + x(n_1C_1 + n_2C_2 + \ldots) + p(\partial V/\partial T)_p + Q_v(\partial x/\partial T)_p.$$

In the case: $G_2 \rightleftharpoons 2G$ (*e.g.*, $N_2O_4 \rightleftharpoons 2NO_2$), $pV = (1 + x)RT$

$$\therefore \quad p(\partial V/\partial T)_p = R[1 + x + T(\partial x/\partial T)_p].$$

From § 88: $\ln px^2/(1 - x^2)\,RT = -\,Q_v/RT + \text{const.}$

$$\therefore \quad (\partial x/\partial T)_p = x(1 - x^2)(Q_v/R + T)/2T^2$$

$$\therefore \quad C_p = (1 - x)C_v + 2xC_1 + R(1 + x) + (x - x^3)/2 \,.\, R(1 + Q_v/RT)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [254]^1$$

The value of the heat of dissociation (Q_p) is usually large in comparison with those of the true molecular heats (C_v and C_1, etc.), so that the apparent specific heat of a [illegible] gas has an abnormally high value, and has also an abnormally high temperature coefficient. Indications of dissociation are shown in the specific heats of many vapours.[2] Berthelot and Ogier[3] measured the specific heats of nitrogen tetroxide and acetic acid vapour. In the first case the molecular heat C_p had the values: 95·1 at 0°, 39·1 at 100°, and 7·1 at 157° (complete dissociation into NO_2).

The *external work* done by a dissociating gas is calculated as follows. The pressures before and after dissociation, p and p', are proportional to the numbers of molecules in a given volume. In the case $G_2 \rightleftharpoons 2G$, for 1 mol of G_2, $p'/p = 1 + x \quad \therefore \delta A = p'dv = pdv + xpdv$. To find dv differentiate the mass-action equation:

$$K = x^2/(1 - x)v \quad \therefore dv = x(2 - x)dx/K(1 - x)^2.$$

Also: $p = RT/v = RTK\,(1 - x)/x^2 \qquad v = x^2/K(1 - x)$

$$\therefore \quad A_T = \int_{v_1}^{v_2} p'dv = RT\left[\ln\frac{v_2}{v_1} + x_2 - x_1 - \ln\frac{1 - x_2}{1 - x_1}\right]$$

$$= RT\left[x_2 - x_1 - 2\ln\frac{x_1(1 - x_2)}{x_2(1 - x_1)}\right] \quad . \quad . \quad . \quad . \quad [255]$$

EXAMPLES XIII.

1. For the reaction $N_2 + O_2 = 2NO$, $K = [NO]^2/[N_2][O_2]$ is given by the relation $\log_{10}\sqrt{K} = \log 0{\cdot}0249 — 2{\cdot}148\,(2200 - T)/T$. Calculate the free energy change of the reaction at 1000° K.

2. According to Haber, $K = [CO_2][H_2]/[H_2O][CO]$ for the reaction

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[1] Cf. Duhem, "Mécan. Chim.," II., 312 ff.; Swart, *Z. p. C.*, 1891, **7**, 120; Schreber, *ibid.*, 1897, **24**, 651; Usherwood, *C. S.*, 1922, **121**, 1604; Einstein, *B. B.*, 1920, p. 380; Keutel, *Diss.*, Berlin, 1911; Selle, *Z. p. C.*, 1923, **104**, 1.

[2] Wiedemann, *A. P.*, 1877, **2**, 195.

[3] *A. C. P.*, 1883, **30**, 382, 400.

$H_2O + CO = CO_2 + H_2$ is given by the equation $\log_{10} K = -2116/T + 0{\cdot}783 \log_{10} T - 0{\cdot}00043T$. The heat of the reaction $CO + \frac{1}{2}O_2 = CO_2$ is 68,000 cals. at 18° C. Find (i.) the heat of the reaction $H_2O + CO = CO_2 + H_2$ at 18° C. (Berthelot found this to be 10,100 cals. experimentally); (ii.) The composition of the water-gas ($CO_2 + H_2 + CO + H_2O$) formed at equilibrium at 1000° K.; (iii.) The temperature at which the product contains 10% CO; (iv.) The heat of combustion of H_2.

3. The equilibrium constant for the dissociation $NO \longrightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$ is $9{\cdot}16 \times 10^{-3} = [NO]/[N_2]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}$ at 1811° K, and $24{\cdot}2 \times 10^{-3}$ at 2195° K. Calculate the heat of combination of $\frac{1}{2}N_2$ and $\frac{1}{2}O_2$ over this range of temperature. If 0·35% NO is formed from the elements at 1811° K., find the amount formed at 2195° K.

4. Calculate the affinity of O_2 for Ni if at 450° C. the partial pressure of O_2 over NiO is $5{\cdot}181 \times 10^{-26}$ mm.

5. Calculate the affinities of oxygen at 25° C. for stannous and stannic tin if the oxygen pressure of these oxides is $6{\cdot}771 \times 10^{-14}$ mm. and $2{\cdot}107 \times 10^{-13}$ mm. respectively.

6. The partial pressure of atmospheric O_2 over FeO at 727° C. is 3×10^{-18} mm. Calculate the affinity of Fe for O_2 at this temperature.

7. The heat of formation of Mn_3O_4 from its elements is 328,000 gm. cals. (Le Chatelier). Assuming this to be independent of temperature, find the temperature at which this oxide would dissociate into its elements when heated in air, if the dissociation pressure of Mn_3O_4 is $2{\cdot}941 \times 10^{-25}$ mm. at 450° C.

8. For the reaction $N_2O_4 \rightleftarrows 2NO_2$ Haber gives the following figures for $K_p = p_{N_2O_4}{}^{\frac{1}{2}}/p_{NO_2}$ under a pressure of 1 atmosphere.

t° C. =	0	18·3	49·9	73·6	99·8
K_p =	8·06	3·71	1·116	0·544	0·273

Plot a graph of K_p against t and use it to show that N_2O_4 is 50% dissociated at 64° C. when the pressure is 1 atm.

9. Find the heat of dissociation of HI into H_2 and I_2 between 300° C. and 320° C. given that $K = [H_2][I_2]/[HI]^2 = 1{\cdot}25 \times 10^{-2}$ and $1{\cdot}3 \times 10^{-2}$ respectively at the two temperatures. (Assume the heat to be constant throughout the range given.)

10. In the reaction $Fe_3O_4 + 4H_2 \rightleftarrows 3Fe + 4H_2O$ at 900° C., $p_{H_2} = 71{\cdot}8$ mm. and $p_{H_2O} = 49{\cdot}3$ mm. at equilibrium. Find $p_{H_2O}{}^4/p_{H_2}{}^4 = K$. The value of K at 727° is $(0{\cdot}57)^4$, at 1025° $(0{\cdot}78)^4$, and at 1150° $(0{\cdot}86)^4$. Find the heat of reaction in three temperature intervals.

11. Calculate the degree of dissociation of CO_2 into CO and O_2:

(i.) At a temperature of 17° C. and a pressure of 1 atm.
(ii.) At a temperature of 2227° C. and a pressure of 0·01 atm.

given that the degree of dissociation is $1{\cdot}58 \times 10^{-5}$% at 1000° K., and that

$$\bar{C}_v \text{ for } CO_2 = 5{\cdot}106 + 0{\cdot}00334T - 7{\cdot}35 \times 10^{-7}T^2$$
$$\bar{C}_v \text{ for } CO = \bar{C}_v \text{ for } O_2 = 4{\cdot}68 + 0{\cdot}000268T.$$

12. The dissociation pressure of $CaCO_3$ is 255 mm. Hg at 740° C., and 678 mm. at 810° C. What is the heat of the reaction $CaO + CO_2$? At what temperature will the dissociation pressure of $CaCO_3$ equal the partial pressure of CO_2 in a mixture of 3 vols. N_2 + 2 vols. CO_2?

13. Bodenstein found that x, the degree of dissociation of gaseous HI, is the following function of temperature: $x = 0{\cdot}13762 + 0{\cdot}0000722t + 0{\cdot}0_6 25764t^2$, t being in °C. If $K = [H_2][I_2]/[HI]^2$ find the heat of dissociation over the range of temperature 380°—400° C. per mol of HI.

14. Nernst and Wartenberg (1906) give the equation $\log_{10} K = 15{\cdot}48 - 29{,}600/T + 2{\cdot}93 \log_{10}(T/1000) - 1{\cdot}286 \times 10^{-3}(T - 1000) + 1{\cdot}61 \times 10^{-7} (T^2 - 1000^2)$ for the equilibrium constant K of the reaction $2CO_2 \rightleftharpoons 2CO + O_2$. ($K = [CO]^2[O_2]/[CO_2]^2$.) Calculate the percentage dissociation of CO_2 at (i.) 1000° K. and 10 atm., (ii.) 1000° K. and 0·01 atm., (iii.) 2500° K. and 10 atm., (iv.) 2000° K. and 1 atm.

Find also at what pressure CO_2 is 50% dissociated at a temperature of 600° K. and also the temperature at which 50% dissociation takes place under a pressure of 0·01 atm.

15. Calculate the percentage dissociation of CO_2 into CO and O_2 at 2000° C. and 1 atm. from the data given in § 85. (Plot log K against 1/T and interpolate.) Calculate also the heat of reaction.

16. Keyes and Hara (1922) found that the pressure of oxygen p (in atm.) in equilibrium with Ag_2O and Ag was dependent on the temperature according to the equation : $\log p = -(2859/T) + 6{\cdot}2853$. Find an expression for the heat of the reaction $2Ag_2O = 4Ag + O_2$ in cals. per mol of O_2 if the densities of Ag_2O and Ag are 7·5 and 10·5 respectively (assumed independent of temperature).

17. Bodenstein and Starck[1] give for the dissociation of $I_2 \rightleftharpoons 2I$ the following values of $K = c_I{}^2/c_{I_2}$:

T° K.	K × 10³.	T° K.	K × 10³.
1073	0·129	1373	4·36
1173	0·492	1473	10·2
1273	1·58		

Find Q_v for the reaction.

18. The degree of dissociation of PCl_5 at 1 atm. is 0·485 at 200° C., and 0·800 at 250° C. Find the heat of dissociation at constant pressure and at constant volume in the interval 200°—250° C.

19. The value of $[SO_2]^2 \times [O_2]/[SO_3]^2$ at 627° C. is $0{\cdot}0_3316$; at 727° C., $0{\cdot}0_2354$, and at 832° C., 0·0280. Find Q_p for the intervals 627°—727° and 727°—832°. Obtain an equation of the form $\log K = A + B/T$. What fraction of SO_3 is dissociated at 1000° C. at 1 atm. ?

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[1] *Z. E.*, 1910, **16**, 961.

CHAPTER XIV

Chemical Equilibrium in Solutions

90. Solutions.—In a solution containing n components the energy depends not only on T and v (or p), as in the case of a fluid of unvarying composition, but also on the proportions of the constituents. A small change in the latter, *e.g.*, a chemical reaction, will bring about small changes of the energy if the initial system is in stable equilibrium.

The only independent variations which the homogeneous system can undergo are those of the masses $m_1, m_2, \ldots$ of the constituents, the total volume V, and the variations produced by adding or withdrawing heat, *i.e.*, variations of entropy. The state of the homogeneous system can, therefore, be completely defined by the masses, $m_1, m_2, \ldots$, the total volume, V, and the total entropy, S:

$$\therefore \qquad U = f(S, V, m_1, m_2, m_3, \ldots)$$

$$\therefore\ dU = (\partial U/\partial S)dS + (\partial U/\partial V)dV + (\partial U/\partial m_1)dm_1 + (\partial U/\partial m_2)dm_2 + \ldots$$

When the masses are constant the system behaves as a simple fluid, for which (§ 70): $dU = TdS - pdV$

$$\therefore\ (\partial U/\partial S) = T;\ (\partial U/\partial V) = -p.$$

Hence $dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots$

where:
$$\mu_1 = (\partial U/\partial m_1)_{S, V, m_2, m_3, \ldots} \quad \ldots \quad (256)$$

is called the *chemical potential* of the first component in the system; μ_2 is the chemical potential of the second component, and so on.

$$dF = d(U - TS) = -SdT - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots$$

$$\therefore \qquad \mu_1 = (\partial F/\partial m_1)_{T, V, m_2, m_3, \ldots} \quad \ldots \quad (256a)$$

$$dZ = d(U - TS + pV) = -SdT + Vdp + \mu_1 dm_1 + \mu_2 dm_2 + \ldots$$

$$\therefore \qquad \mu_1 = (\partial Z/\partial m_1)_{T, p, m_2, m_3, \ldots} \quad \ldots \quad (256b)$$

Equations (256) to (256b) give alternative definitions of the chemical potential.

Let a virtual chemical change:

$$n_1A_1 + n_2A_2 + \ldots \longrightarrow n_1'A_1' + n_2'A_2' + \ldots$$

occur to a small extent, and let:

$dm_1 = M_1 . n_1 . d\lambda$; $dm_2 = M_2 . n_2 . d\lambda$; etc., where $d\lambda$ is a small *arbitrary* (positive) magnitude defining the *extent* of the change. M is the molecular weight. Then:

$$\delta F = - SdT - pdV + d\lambda \Sigma n_1 M_1 \mu_1.$$

The *condition for equilibrium,* when T and V are constant ($dT = 0$; $dV = 0$) is $\delta F = 0$, hence: $\Sigma n_1 \mu_1 M_1 = 0$.

The same result is found when T and p are constant ($\delta Z = 0$).

Put $M_1\mu_1 = \bar{\mu}_1$, the *molar chemical potential,* then:

$$\Sigma n_1 \bar{\mu}_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (257)$$

Equation (257) shows that the condition of equilibrium at constant temperature, and constant pressure or volume, is given by writing down the chemical equation of the reaction but substituting the chemical potential instead of the chemical symbol.

If $n_2 = n_3 = \ldots = 0$, we have a *pure substance,* and in this case we see that the chemical potential is the thermodynamic potential per unit mass (or mol).

The above equations, deduced by Gibbs,[1] are perfectly general and apply to all solutions, whether dilute or not.

In the case of a *gaseous system* we deduced [234]:

$$F = \Sigma n_1 g_1(T) - RT\Sigma n_1 \ln V/n_1$$

$$= \Sigma n_1 g_1(T) + RT\Sigma n_1 \ln c_1, \text{ where } c_1 = \text{concentration} = n_1/V$$

$$\therefore \quad (\partial F/\partial n_1)_{T,\,V,\,n_2,\,n_3,\ldots\ldots} = g_1(T) + RT \ln c_1 \quad . \quad . \quad [258]$$

giving the *chemical potential* of a component in an ideal gas mixture.

We have shown (§ 53) that in *dilute solutions* the equation representing the state of the solute is the same as that of an ideal gas, and we can put similarly:

$$\bar{\mu}_1 = G_1(T) + RT \ln c_1 \quad . \quad . \quad . \quad . \quad . \quad [259]$$

where $G_1(T)$ is an unknown function of temperature, different from that in [234]. Equation [259] then gives as the *condition of equilibrium* at constant temperature and volume: $RT\Sigma n_1 \ln c_1 + \Sigma n_1 G_1(T) = 0$, where $\Sigma n_1 G_1(T)$ depends only on the temperature and chemical composition of the solution, and can be put equal to $-$ RT ln K, a *function of temperature* for the given system. Thus:

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[1] "Scientific Papers," Vol. I., p. 92; Bródy, *A. P.*, 1914, 44, 585.

$$\Sigma n_1 \ln c_1 = \ln K \quad . \quad . \quad . \quad . \quad . \quad . \quad [260]$$

or

$$c_1^{n_1} c_2^{n_2} \ldots = K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [260a]$$

Thus, *the law of mass action holds for dilute solutions.*

As a further example of the application of the chemical potential consider a solid in contact with its saturated solution:

	satd. sol. of salt +	crystals of solid salt
Potential	Z'	Z''

Let a mass δm of salt pass into solution (a virtual change), at constant pressure.

Potential of solution increases by $\delta Z' = (\partial Z'/\partial m)\delta m$.

Potential of solid increases by $-(\partial Z''/\partial m)\delta m = \delta Z''$.

Total change of thermodynamic potential $= \delta Z = \delta(Z' + Z'') = \delta Z' + \delta Z'' = \delta m(\partial Z'/\partial m - \partial Z''/\partial m)$.

There will be equilibrium when $\delta Z = 0$ (T and p constant), *i.e.*, when

$$\partial Z'/\partial m = \partial Z''/\partial m, \qquad \text{or} \qquad \mu' = \mu''.$$

That is, *the chemical potentials of the salt in the solid state and in solution must be equal.* This equality of chemical potential of a component in all the phases of a system is the general condition of equilibrium in heterogeneous systems.

For a given salt, μ'' is constant, hence μ' is constant, at a fixed temperature and pressure, *i.e.*, c is constant in presence of the solid salt.

We can also apply the same method to a substance dissolved in two solvents (1) and (2) which do not mix, and so deduce the distribution law (§ 92).

Alternative Deduction of the Law of Mass Action for Solutions.—The method used for gases (§ 83) may be applied to solutions. The whole apparatus is now immersed in a bath of pure solvent, and the different components are contained in solution in cylinders fitted with pistons permeable only to solvent. The cylinders are separated from the equilibrium box by septa permeable only to the substances dissolved, and instead of gas pressures in § 83 we now have to consider osmotic pressures.

It may now be necessary to consider free ions in separate solutions, *e.g.*, in the case $NaCl \rightleftharpoons Na^{\cdot} + Cl'$.

The work obtained in a reversible change of concentration is:

$$A_T = \int_{V_1}^{V_2} P dV = P_2V_2 - P_1V_1 - \int_{P_1}^{P_2} V dP \quad \text{per mol.}$$

But $P_1V_1 = P_2V_2$ (ideal solutions), hence:

$$A = -\int_{P_1}^{P_2} V dP = -RT \int_{P_1}^{P_2} dP/P = RT \ln (P_1/P_2) = RT \ln (c_1/c_2).$$

Free Concentrations.			Work of Change.		Equilibrium Concentrations.
$Na^{\cdot}$	C_1	→	$RT \ln (C_1/c_1)$	→	c_1
Cl'	C_2	→	$RT \ln (C_2/c_2)$	→	c_2
NaCl	C_3	←	$-RT \ln (C_3/c_3)$	←	c_3

The work done in introducing 1 mol of $Na^{\cdot}$ and 1 mol of Cl' into the box, at the equilibrium concentrations, and in removing 1 mol of NaCl, is $- RT - RT + RT = - RT$. The work done in changing the free concentrations, at which the substances are given, to the equilibrium concentrations in the box, is given in the three cases in the above table. Hence:

$$\begin{aligned} A_T &= RT [\ln (C_1/c_1) + \ln (C_2/c_2) - \ln (C_3/c_3)] - RT \\ &= RT \ln (c_3/c_1c_2) + RT \ln (C_1C_2/C_3) - RT \\ &= RT \ln K - RT\Sigma n_1 \ln C_1 + RT\Sigma n_1 \text{ in the general case.} \end{aligned}$$

The second term is, with given values of the C's, constant at a given temperature and pressure, and since A_T depends only on T, *p*, and the C's, it follows that K is constant. Thus the law of mass action holds for dilute solutions.[1]

By the method of § 86 we then find:

$$d \ln K/dT = Q_v/RT^2 \quad . \; . \; . \; . \; . \quad [247]$$

The applications of the law of mass action to solutions will be found in the appropriate treatises. It will be sufficient to mention that, in the case of strong acids and strong bases, which are assumed to be completely ionised at infinite dilution, the reaction of neutralisation is in all cases the union of hydrogen and hydroxide ions (possibly hydrated) to form practically unionised water:

$$H^{\cdot} + OH' = H_2O.$$

This reaction takes place with the evolution of 13·7 kgm. cal.[2]

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[1] On the methods of deduction cf. Porter, *F. S.*, 1920, **15**, 75.

[2] Richards and Rowe, *J. A. C. S.*, 1922, **44**, 684, find the value at 20° to be 13·62 to 13·69 20°-kg. cal. The differences with different acids and bases are within the limits of error.

91. Equilibrium in Solutions of Electrolytes.—The application of the mass action equation to the dissociation of a binary electrolyte leads to the following equation:

$$a^2/(1 - a)V = K_1$$

where a = degree of dissociation, V = volume containing 1 mol of solute, and K_1 = a constant. On the assumption that $a = \Lambda/\Lambda_\infty$, the following equation is obtained:

$$\Lambda^2/\Lambda_\infty(\Lambda_\infty - \Lambda)V = K_1$$

where Λ = equivalent conductivity of the solution at dilution V and Λ_∞ = limiting value of Λ when $V \rightarrow \infty$.

The thermodynamic derivation of these equations precludes their application except where the solute is in a state analogous to an ideal gas, *i.e.*, when the regions of solvent influenced by individual molecules of solute are independent of each other, a condition more likely to hold at high than at low dilutions.

Ostwald, who deduced the above equation, confirmed it for 250 organic acids,[1] all weak, and Bredig[2] for 50 weak organic bases. The fourth column in the following table shows that in the case of acetic acid there is fair agreement at the higher dilutions.

Acetic Acid in Aqueous Solution at 25° C.

V (litres).	Λ.	a.	$K_1 \times 10^6$.	η (viscosity).	$K_1' \times 10^6$.	$K_1'' \times 10^6$.
·334	·6186	·001595	7·7	1·347	13·9	16·5
·672	1·123	·002896	12·5	1·169	17·2	18·6
·989	1·443	·003636	14·0	1·112	17·4	18·4
1·977	2·211	·005701	16·5	1·056	18·3	18·8
5·374	3·804	·009806	18·1	1·021	18·8	19·0
10·753	5·361	·01382	18·0	1·010	18·4	18·5
24·875	8·388	·02163	19·2	1·004	19·5	19·5
63·26	13·03	·03359	18·5	1·002	18·6	18·6
∞	387·9	1·00000	—	1·000	—	—

To extend the agreement, a correction may be made for the change with concentration of the viscosity of the solution, assuming Λ to be inversely proportional to the viscosity, *i.e.* $\alpha = \eta\Lambda/\eta_\infty\Lambda_\infty$. The results are shown as K_1'. Kendall,[1] introducing the solvent concentration into the mass action expression, corrects this value to K_1'', obtaining still better agreement. Solutions of *strong electrolytes* (*i.e.*, those largely ionised in solution), however, show no conformity with the equation and many equations have been proposed to apply to them, some entirely, others partly, empirical.

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[1] *Z. p. C.*, 1888, **2**, 270; 1889, **3**, 170, 241, 369.

[2] *Ibid.*, 1894, **13**, 289.

Rudolphi[2] suggests $\alpha^2/(1 - \alpha)\sqrt{V}$ = const., and van't Hoff,[3] $\alpha^{3/2}/(1 - \alpha)V$ = const. A generalised form of such equations, due to Storch,[4] has found some favour, viz.: $C_1{}^m/C_0 = K'$, where C_1 = concentration of either ion; C_0 = concentration of undissociated molecules, and K', m, are constants.

The various attempts to give a theoretical explanation of the "anomaly of strong electrolytes," and, in general, to bring the behaviour of electrolytes into a wide and fairly simple scheme, may be placed in five groups.[5]

According to the first group, the errors incident to conductivity measurements are supposed to be large enough to produce the observed deviations. This devolves into a criticism of the work of Kohlrausch and Maltby, who determined with the greatest care the values concerned, but recent experiments by Weiland,[6] conducted with extreme accuracy, on the conductivity of potassium chloride solutions at very high dilutions show not only that this criticism is unfounded, but that at concentrations between 0·00001 and 0·0001N the Ostwald equation holds good. This had already been inferred by Arrhenius from the results of Kohlrausch and Maltby.

The second idea is that changes with concentration of ionic mobility, etc., render the method of calculating the degree of dissociation inaccurate.

The third explanation is that discrepancies are due to the formation of complex ions.

Ghosh[7] extended Sutherland's idea that the theory of a partial dissociation into ions is inaccurate. Making a number of postulates, among them that ions in a solution are arranged in a space-lattice, he deduced an equation for each class of electrolytes containing only fundamental quantities. For a univalent binary electrolyte he obtained:

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[1] *J. A. C. S.*, 1914, **36**, 1069.

[2] *Z. p. C.*, 1895, **17**, 385.

[3] *Ibid.*, 1895, **18**, 301.

[4] *Ibid.*, 1896, **19**, 13.

[5] Partington, *C. S.*, 1910, **97**, 1158; *F. S.*, 1919, **15**, 98. A summary is given in these two papers of all but the very recent work on the dilution law.

[6] *J. A. C. S.*, 1918, **40**, 131.

[7] *C. S.*, 1918, **113**, 449, 627, 707, 790; 1920, **117**, 823, 1390.

$$\frac{N_0 e^2 \sqrt[3]{2N_0}}{D\sqrt{V}} = 2RT \ln \frac{\Lambda_\infty}{\Lambda}$$

where N_0 = Avogadro's constant; e = electronic charge; R = gas constant; D = dielectric constant of medium; T = absolute temperature and V = dilution in c.cs. The ions exert electrostatic forces on one another and are completely free only when their kinetic energies exceed a certain value. A noticeable feature in Ghosh's theory is that it is assumed that each molecule exists in a state of *partial* dissociation which may be anything between 0 and unity, but will have an average value of a. This theory has been criticised by Partington,[1] Kendall,[2] and others, largely on account of Ghosh's methods of obtaining agreement between the observed values (which he sometimes alters to suit his results) and those calculated from his equations. The latter must be regarded as empirical and not very accurate.

On the assumption that the unmodified mass action law may not be applicable to ionisation, a number of dilution equations have been deduced or put forward empirically. According to Arrhenius $C_1^2/C_0 = f(C_1)$, where C_1 = concentration of either ion and C_0 = concentration of undissociated binary electrolyte. Partington [3] deduced the following equation for moderately strong electrolytes: $a^2/(1 - a)(V + \epsilon a) = K$, where ϵ is a constant for each electrolyte and K is the corrected Ostwald K_1. Kendall [4] has put forward a special case of this equation: $a^2/(1 - a)V = k'[(1 - a)/a] + K_1$. These fit the results for electrolytes of medium strength. Another variation has been used by McDougall [5] and by Kraus and Bray [6]: $a^2/(1 - a)V = K_1 + k(a/V)^n$, where n is a constant < 1. Szyszkowski [7] deduces $a^2/(1 - a)V = K_1 + k[(1 - a)/V]^P$, where P is a constant for each electrolyte. The last two equations apply to strong electrolytes.

A method of approaching the subject, which has been used principally by American physical chemists, has been to fit observed data to the ordinary mass law by introducing an arbitrary conception known as the *activity coefficient* of an electrolyte.[1] The idea is to replace van't Hoff's law $P = RTc$ by the equation $P = RT\boldsymbol{a}$, $\boldsymbol{a}$, the "activity," replacing the concentration term for molecules or ions. The mass action expression becomes: $a_1a_2 = Ka_0$ for a binary electrolyte, where a_1, a_2 represent the activities of the ions, and a_0 that of the undissociated molecules. At infinite dilution the activity of each ion is considered equal to its concentration. In the absence of reliable data as to the concentration of undissociated salt it is convenient to choose the standard state of the substance so that K becomes unity, or: $a_1a_2 = a_0$. Then a_0 is the activity of the electrolyte and the geometrical mean of the ionic activities is given by $a_0^{\frac{1}{2}}$.

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[1] *F. S.*, 1919, **15**, 98.
[2] *J. A. C. S.*, 1922, **44**, 717.
[3] *C. S.*, 1910, **97**, 1158.
[4] *C. S.*, 1912, **101**, 1275.
[5] *J. A. C. S.*, 1912, **34**, 385.
[6] *Ibid.*, 1913, **35**, 1315.
[7] *M. K. N.*, 1913, **2**, No. 41.

Several methods have been used to measure activities. Instead of Nernst's equation [307] for the E.M.F. of a concentration cell, $E = 2(RT/yF)\ln a'c'/a''c''$, where R = gas constant, T = abs. temperature, y = valency of electrolyte, a = degree of dissociation (Λ/Λ_∞) and c = concentration of electrolyte, the equation $E = 2(RT/yF)\ln f'c'/f''c''$ has been used, where $f = a/c$, the "activity coefficient." The activity coefficient found by this method is in general, for strong electrolytes at moderate dilutions, considerably different from a, the degree of dissociation defined as Λ/Λ_∞, as the following table shows:

HYDROCHLORIC ACID SOLUTION IN WATER.

Conc.	18° C. $a = \Lambda/\Lambda_\infty$.	25° C. f (activity coefft.).
0	1·000	1·000
·0005	—	·991
·001	·990	·984
·005	·981	·947
·01	·972	·924
·05	·944	·860
·1	·925	·814
·5	—	·762
1·0	—	·823
5·0	—	2·51
10·0	—	10·65

92. The Distribution Law.—Berthelot and Jungfleisch (1872),[2] as a result of experiments, concluded that when a substance is brought in contact with two immiscible liquids, in each of which it is soluble, the quantities dissolved by the two liquids are in a constant ratio, independent of the relative volumes of the liquids, and called the *distribution coefficient*, *k*. Two solutes are distributed between a pair of solvents as if each solute were present alone.

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[1] For a summary of work on "activity" of electrolytes, see Lewis and Randall, *J. A. C. S.*, 1921, **43**, 1112.

[2] *A. C. P.*, 1872, **26**, 417.

Berthelot and Jungfleisch considered that *k* depended on the concentration of the shared substance. It was shown, however, by Nernst[1] and by Aulich,[2] that for a solute which does not alter its molecular weight in passing from one solvent to the other, *k* should be independent of concentration, but will depend on temperature.

It is assumed that equilibrium can subsist with a specified pair of solvents and a solute distributed between them in any *one* ratio of concentration : c_1/c_2, where 1 and 2 refer to the two solvents. We have to prove that for *all* concentrations within the range of application of the laws of dilute solutions :

$$c_1/c_2 = const. = k \quad . \quad . \quad . \quad . \quad . \quad . \quad [261]$$

Let two cylinders contain the pairs of solvents, in which the same solute exists under the osmotic pressures P_1,P_2 in the first,

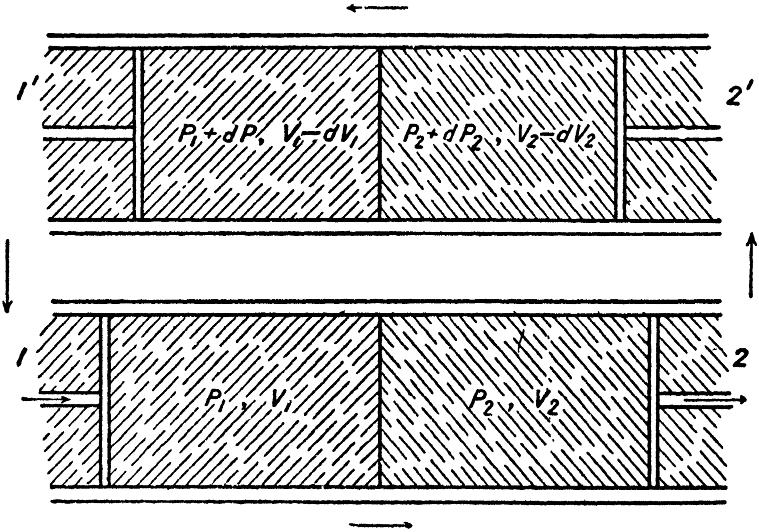

FIG. 30.

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[1] Z. p. C., 1890, **6**, 37 ; 1891, **8**, 110.

[2] Z. p. C., 1891, **8**, 105 ; cf. Schilov, Lepin, Jantschak and Dubinin, *ibid.*, 1922, **101**, 353 ; Jakowkin, *ibid.*, 1895, **18**, 585.

and $P_1 + dP_1$, $P_2 + dP_2$ in the second; and let V_1, V_2, and $V_1 - dV_1$, $V_2 - dV_2$ be the corresponding volumes of solution containing 1 mol of solute (Fig. 30). The cylinders are closed by pistons 1 and 1′ permeable to solvent 1 only, pistons 2 and 2″ to solvent 2 only.

(1) Press in piston 1 so that 1 mol of solute passes from the V_1 space to the V_2 space across the plane of contact, at the same time allowing piston 2 to move out so that the concentrations are unaltered. The work done is:

$$[1] = -P_1V_1 + P_2V_2.$$

(2) The volume V_2 of the second solution containing 1 mol of solute is isolated, and the volume dV_2 of solvent removed through the semipermeable piston. The work done is:

$$[2] = -P_2dV_2.$$

(3) The resulting solution is mixed with identical solution in 2′, and 1 mol of solute passed into the $V_1 - dV_1$ space, the work done being:

$$[3] = (P_1 + dP_1)(V_1 - dV_1) - (P_2 + dP_2)(V_2 - dV_2).$$

(4) The concentration in the $V_1 - dV_1$ space is now changed to that corresponding with V_1, the work done being:

$$[4] = P_1dV_1$$

and the resulting solution is returned to the initial compartment.

An isothermal reversible cycle has been completed, hence by (44):

$$[1] + [2] + [3] + [4] = 0 \quad \therefore \quad V_1dP_1 = V_2dP_2.$$

But $P = cRT$ [153a], $V_1/V_2 = c_2/c_1$, and $dP = RTdc$

$$\therefore \quad dc_1/c_1 = dc_2/c_2, \text{ or } dc_1/c_1 - dc_2/c_2 = 0.$$

By integration: $\ln c_1 - \ln c_2 = f(T)$ or $c_1/c_2 = \mathit{const.} = k$ at a particular temperature.[1]

93. Depression of Solubility.

The addition of a third substance to *one* of two partially miscible liquids reduces the solubility of that liquid in the other.[2] Let ether and water be taken, and let s denote the solubility of pure ether in water. Now let a third substance, insoluble in water, say benzene, be added to the ether. The solubility of ether in the aqueous layer must equal that of ether vapour, and the latter is related to the vapour pressure by Henry's law: $p : p' = s : s'$. But, from [155a]:

$$\ln (p/p') = n/N$$

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[1] On alteration of k with temperature: MacDougall, *J. A. C. S.*, 1919, **41**, 1718.

[2] Nernst, *Z. p. C.*, 1890, **6**, 16.

where n = number of mols of substance, and N = number of mols of ether, in the solution. Thence :

$$n/N = \ln(p/p') = \ln(s/s') = (s - s')/s', \text{ approximately,}$$

or

$$(s - s')/s = n/(n + N) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [262]$$

The molecular weight of the added substance (*e.g.*, benzene) may thus be calculated from the change in solubility of the ether in water. The latter may be found by comparing the freezing-points of the aqueous layer in the two cases.

94. Dilute Solid Solutions.—The theory of depression of freezing-point given in § 57 assumes that the solid separating is *pure* frozen solvent. In this case the freezing-point is a function of the concentration of the liquid phase, but not of the composition of the solid, since the latter remains constant.

In some cases the solid which separates is a homogeneous solid solution of both components. The effect on the freezing-point of a solvent when a solid solution separates requires further investigation.[1] In this case Fig. 24 is replaced by Fig. 31, in which the single vapour pressure curve of the solid is replaced by the vapour pressure curves of the solid solutions. AB, BC are the vapour pressure curves of pure solid and liquid solvent, respectively, B(T_1) being the freezing-point of pure solvent. B_2C_2 is the vapour

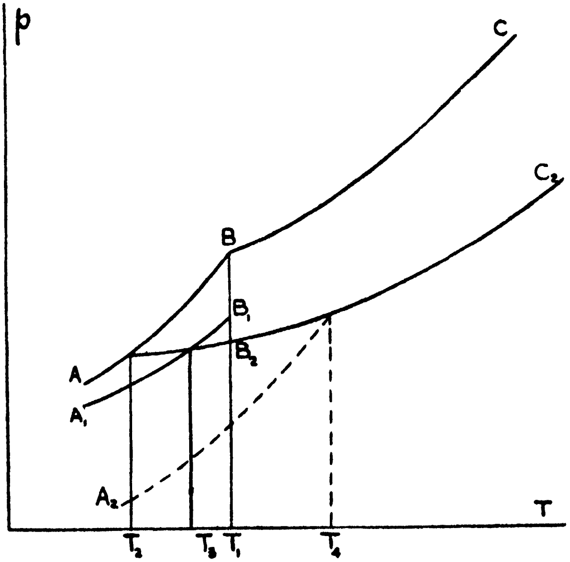

Fig. 31.

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[1] Van't Hoff, *Z. p. C.*, 1890, **5**, 322.

pressure curve of a liquid solution, and if pure solvent separates on freezing, the freezing-point is T_2, and the depression $T_1 - T_2$. But if the *solid* solvent dissolves some of the second (non-volatile) component, its vapour pressure is lowered, and the vapour pressure of the solid phase will now be represented by the curve A_1B_1 instead of AB. The freezing-point is T_3, corresponding with the intersection of A_1B_1 and B_2C_2. The depression $T_1 - T_3$ is obviously smaller than in the case when pure solvent separates, and in some cases the freezing-point may actually be *raised*, the intersection lying to the right of T_1, as at T_4.

If the lowering of vapour pressure is proportional to the concentration, both in the liquid and solid solutions:

$$B_1B_2/BB_2 = (c_2 - c_1)/c_2$$

where c_1 and c_2 are the concentrations of solute in the solid and liquid solutions, respectively. Thus the freezing-point will lie to the right (T_4), or to the left (T_3) of T_1 according as c_1 is greater or less than c_2, respectively. We thus arrive at an important rule deduced by Roozeboom: the concentration of that component, by addition of which the freezing point is depressed, is greater in the liquid than in the solid phase, and the concentration of that component, by the addition of which the freezing-point is raised, is greater in the solid than in the liquid phase.

If the solid separating on freezing has the same composition as the liquid, the freezing-point concentration curve will at that point have a maximum or a minimum.[1]

95. **Heats of Solution and Dilution.**—When 1 mol of solute B dissolves in x mols of solvent A, and the solution is brought to the initial temperature, the amount of heat *absorbed*, called the *integral heat of solution* per mol of B: $Q(xA,B) = Q_x$, is a function of x and of temperature (the effect of pressure is negligible).

The heat of solution in a very large amount of solvent, when further addition of *solvent* produces no thermal change, may be called the *heat of dilute solution*, Q_∞.

When a further x_2 mols of solvent are added to a solution containing 1 mol of solute and x_1 mols of solvent, the heat of dilution is $Q_{x_2} - Q_{x_1}$.

If Q_x is represented graphically as a function of x at a given temperature, the heat of dilution is the difference of the ordinates at x_1, and at $(x_1 + x_2)$. The slope of the tangent to the curve at x is the *differential heat of dilution* :

---

[1] On the thermodynamic theory of solid solutions see Roozeboom, *Z. p. C.*, 1899, **30**, 385; Whetham, "Theory of Solution," 1902, pp. 62 ff.; also, generally, Findlay, "Phase Rule," and Bruni, "Feste Lösungen," 1901. *Applications:* Desch, "Metallography."

$$\partial Q_x/\partial x = Q_d.$$

It is very approximately equal to $Q_{x+1} - Q_x$.

Example 1.—Thomsen found that the (almost saturated) solution of composition $CuCl_2 + 10H_2O$ ($x = 10$) gave on dilution at 18° C. the following *evolutions* of heat :

Mols H_2O added (x) .	10	20	40	90	190
Heat evolved . .	1606	2430	3308	4052	4510 cal.

These values are represented by the equation $5023x/(x + 21{\cdot}24)$. Hence, on infinite dilution the heat evolved will be 5023 cal.

The heat of solution of $CuCl_2$ in $200H_2O$ is 3710 cal. (evolved), according to Reicher and van Deventer. From the formula :

Heat of dilution from $10H_2O$ to infinity $= 5023$ cal.
Also heat of dilution from $10H_2O$ to $200H_2O = 4510$ cal.

$\therefore$ heat of dilution from $200H_2O$ to infinity $= 513$ cal., $\therefore$ heat of solution of $CuCl_2$ in an infinite amount of water $= 3710 + 513 = 4223$ cal. The heat of solution of $CuCl_2, 2H_2O$ in $8H_2O$ is $4223 - 5023 = -800$ cal. (absorbed). The salt dissolves in a nearly saturated solution with absorption of heat.[1]

We may also consider the heat absorbed (or evolved) when y mols of solute B dissolve in 1 mol of solvent A. This may be denoted by $Q(A,yB) = Q_y$.

If x' and y' are the values corresponding with saturation, the heat of formation of 1 mol of saturated solution is $Q_x'/(1 + x') = Q_y'/(1 + y')$. If to a solution containing y_1 mols of solute a further y_2 mols are added, the heat absorbed will be $Q_{y_1+y_2} - Q_{y_1}$, the difference of the ordinates at y_1 and $(y_1 + y_2)$. The slope of the tangent to the curve at y is the *differential heat of solution* : $\partial Q_y/\partial y = Q_s$. It varies from the initial heat of solution, when 1 mol of solute goes into solution in pure solvent, to λ, the *differential heat of saturation*, the heat of solution when the last mol of solute goes into solution in an indefinite large amount of very nearly saturated solution. This is the heat of solution used in § 75, and is an important magnitude.

It is clear that λ cannot be determined directly, but it may be calculated from the integral heat of solution and the heat of dilution in the following way. Evidently $y = 1/x$ and $Q_y = Q_x/x$; hence :

$$\partial Q_y/\partial y \equiv \lambda = \partial(Q_x/x)/\partial(1/x) = Q_x - x\partial Q_x/\partial x$$
$$= Q_x - xQ_d$$

---

[1] In other cases, also, the differential heat of saturation differs in sign from the integral heat of solution (Reicher and van Deventer, *Z. p. C.*, 1890, **5**, 559).

or: *differential heat of solution = integral heat of solution − differential heat of dilution.*

Example 2.—The quantity of sodium nitrate represented by $Na_2N_2O_6$ requires 10·9 mols H_2O for solution at 18° C. The heat of solution (absorbed) from $12H_2O$ to $400H_2O$ is $5868 + 4700\,(x - 12)/(x + 28{\cdot}96)$. Assume that this holds over the whole range of solubility. Put $x = 10{\cdot}9$, then: Integral Heat of Saturation = 5738 cal. The heat of dilute solution = 5868 + 4700 = 10,568 cal. The heat of dilution of the saturated solution is obtained by differentiating the expression for the heat of solution with respect to x and then putting $x = 10{\cdot}9$: it is $4700 \times 40{\cdot}96/(39{\cdot}86)^2 = 121{\cdot}2$ cal. The limiting heat of saturation is then $5738 - 10{\cdot}9 \times 121{\cdot}2 = 4417$ cal.

Finally, consider the heat of solution of two liquids which mix in all proportions. The heat of formation of any mixture may be calculated by the above methods, but it is convenient to represent the heat of formation of 1 mol of solution as a function of the fractional molecular composition of the mixture, since then the curve is finite, extending from $z = 0$ to $z = 1$, where $z = x/(x + 1) = y/(y + 1)$. Then $Q = Q_x/(x + 1) = Q_y/(y + 1)$.

Example 3.—In the case of mixtures of water with sulphuric acid Thomsen finds the heat (evolved) of admixture of x mols of water with 1 mol H_2SO_4 to be given by: $17860x/(x + 1{\cdot}7983)$.

Put $x = z/(z - 1)$, and divide by $(x + 1) = 1/(1 - z)$, then the heat of formation of the mixture containing the molar fraction z of H_2O is $Q = 9932z\,(1 - z)/(1 - 0{\cdot}4439z)$.

This gives the following table:[1]

Molar fraction $H_2O = z$.	0·2	0·4	0·6	0·8
Heat of formation $= Q$.	1740	2900	3250	2460 cal.

The *vapour pressure of a saturated solution,* in the presence of solid salt, depends only on the temperature, as we see from the phase rule (§ 97, $n = 2$, $r = 3$ $\therefore$ $F = 1$). If 1 gm. of solvent is evaporated under the constant vapour pressure p, the heat of isothermal evaporation is (79):

$$L = T(dp/dT)\,[v''' + sv' - (s + 1)v''] \quad . \quad . \quad . \quad (263)$$

where v', v'', v''' are the specific volumes of the salt, solution, and vapour, respectively, and s = the weight of salt associated with 1 gm. of solvent in the solution.

If v' and v'' are neglected in comparison with v''', and if the vapour is assumed to obey the gas laws, $v''' = RT/Mp$, where M is the molecular weight,

$$\therefore \qquad L = \frac{RT^2}{M}\frac{d\ln p}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [264]$$

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[1] Lehfeldt, "Physical Chemistry," 1899, p. 262; cf. Rümelin, *Z. p. C.*, 1907, **58**, 449; Brönsted, *ibid.*, 1908, **64**, 641; 1910, **68**, 693; Nernst, "Lehrbuch," 8–10 Aufl., pp. 171 ff.

L is the heat *absorbed* when 1 gm. of solvent is evaporated at T and p from a saturated solution, or the heat *evolved* where 1 gm. of solvent *vapour* unites with the requisite amount of salt, s gm., to form a saturated solution.

Let Q_s be the heat *evolved* when the amount of salt s dissolves in 1 gm. of *liquid* solvent to form a saturated solution at p and T, then $Q_s = \mathrm{L} - \mathrm{L}_e$, where L_e is the latent heat of evaporation of pure solvent at p_0, T (see § 57, *note*), *i.e.*,

$$\mathrm{L}_e = \frac{\mathrm{RT}^2}{\mathrm{M}}\frac{d\ln p_0}{d\mathrm{T}}$$

$$\therefore \qquad Q_s = \frac{\mathrm{RT}^2}{\mathrm{M}}\frac{d\ln (p/p_0)}{d\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad [265]$$

an equation due to Kirchhoff (1858).[1]

In considering the *heat of dilution* of a solution of 1 part of solute in x of solvent we may begin with the equation:

$$(dp/d\mathrm{T})_x = \mathrm{L}_x/\mathrm{T}\Delta v$$

where L_x is the latent heat of evaporation of 1 gm. of solvent from an infinite mass of solution. If the vapour is an ideal gas, and we neglect the change of volume of the liquid: $\Delta v = \mathrm{RT/M}p$:

$$\therefore \quad \mathrm{L}_x = \frac{\mathrm{RT}^2}{\mathrm{M}}\left(\frac{d\ln p}{d\mathrm{T}}\right)_x \quad . \quad . \quad . \quad . \quad . \quad . \quad [266]$$

L_x is the heat *evolved* when 1 gm. of solvent *vapour* at p and T is condensed in an infinite amount of solution. The diminution of energy is $\mathrm{L}_x - \mathrm{RT/M}$. The same result is attained by first compressing the vapour to the pressure p_0 of pure solvent, leaving its energy unchanged (§ 33), condensing it to liquid with diminution of energy $\mathrm{L}_e - \mathrm{RT/M}$, changing the pressure of the liquid to p, and adding the 1 gm. of *liquid* solvent to the infinite amount of solution, with the evolution of heat Q_d, the differential heat of dilution. The total diminution of energy is then $\mathrm{L}_e - \mathrm{RT/M} + Q_d$, which must be equal to $\mathrm{L}_x - \mathrm{RT/M}$. Therefore $Q_d = \mathrm{L}_x - \mathrm{L}_e$

$$\therefore \qquad Q_d = \frac{\mathrm{RT}^2}{\mathrm{M}}\cdot\left(\frac{d\ln (p/p_0)}{d\mathrm{T}}\right)_x \quad . \quad . \quad . \quad . \quad . \quad [267]$$

an equation also due to Kirchhoff.[2]

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[1] *A. P.*, 1858, **104**, 612; "Ges. Abh.," 492; Roozeboom, *Z. p. C.*, 1889, **4**, 50; Scholz, *A. P.*, 1892, **45**, 193; Schiller, *ibid.*, 1899, **67**, 292; Jüttner, *Z. p. C.*, 1901, **38**, 76.

[2] *A. P.*, 1858, **103**, 176; Porter, *F. S.*, 1915, **11**, 19; 1918, **13**, 373; Edgar and Swan, *J. A. C. S.*, 1922, **44**, 570. See also F. Jüttner, *Z. p. C.*, 1901, **38**, 76 (full bibliography); Duhem, *ibid.*, 1888, **2**, 568; Ewan and Ormandy, *C. S.*, 1892, **61**, 769; Ewan, *Z. p. C.*, 1894, **14**, 409; 1899, **31**, 22.

When $Q_d = 0$, $(\ln p/p_0)_x =$ const., as in [155a]; von Babo's Law is valid only in this case. A *small* change of $\ln p/p_0$ with T occasions an appreciable value of Q_d and the calculation of Q_d from vapour pressure measurements is difficult, on account of the enormous influence of small errors in p. The calculation of p from Q_d is more accurate.

The integral heat of dilution is

$$Q_{x_2} - Q_{x_1} = \frac{\mathrm{RT}^2}{\mathrm{M}} \int_{x_1}^{x_2} \frac{\partial \ln (p/p_0)}{\partial \mathrm{T}} dx.$$

In Fig. 32 AB = 1, B*a* = *z* parts of constituent B, and A*a* = 1 − *z* parts of constituent A (say, water and sulphuric acid). The corresponding ordinates denote the amounts of heat absorbed by the admixture. These lie on a continuous curve, wholly above (A*b*B) or below (A*β*B), or partly above and partly below, the axis of *z*. The length *ab* represents the heat absorbed in the addition of *z* parts of B to 1 − *z* of A to form unit mass of solution. The heat evolved for 1 part of A will be 1/(1 − *z*) of this, viz., BC. As *z* becomes unity, the point C moves upwards and finally attains the position F, when 1 part of A dissolves in an infinite amount of B. If *b*G is drawn a tangent to the curve, BG represents the heat of solution of 1 part of B in an infinite amount of solution of composition represented by *a*.[1] The corresponding intercept on the A axis is the heat of solution of 1 part of A in the solution.[2]

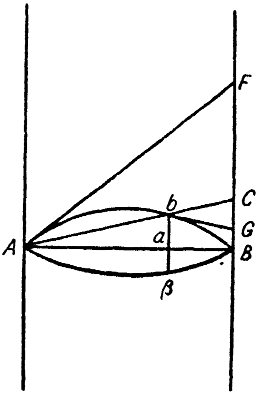

FIG. 32.

96. Effect of Pressure on Solubility.—Let the apparatus described in § 75 be enclosed in a vessel into which an indifferent gas may be pumped to any desired pressure p. If there is a change in total volume when solute passes into solution, it will occasion the performance of work by, or against, the pressure p.

Let P = osmotic pressure under total pressure p; Δv = change in total volume when 1 mol of solute is dissolved, which may be considered constant. Let V = change in volume of solution when solvent is admitted to dissolve 1 mol of solute; this may also be considered as constant. The following cycle is carried out:

(1) Increase p to $p + \delta p$: the work done $= -\delta\mathrm{A}$, say.

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[1] See Roozeboom, "Heterogen. Gleichgewichte," vol. 2.

[2] For heats of dilution, see Tucker, *P. T.*, 1915, **215**, 319; Brönsted, *Z. p. C.*, 1908, **64**, 641; Magie, *P. R.*, 1912, **35**, 265; Pratt, *F.*, 1918, **185**, 663; Deventer and van de Stadt, *Z. p. C.*, 1892, **9**, 43; Stackelberg, *Z. p. C.*, 1898, **26**, 533; Gibbons, *J. P. C.*, 1917, **21**, 48; Bancroft, *ibid.*, 1906, **10**, 319.

For specific heats of solutions, see Bousfield, *P. T.*, 1919, **218**, 119; Richards and Rowe, *J. A. C. S.*, 1920, **42**, 1621; 1921, **43**, 770; Speranski, *Z. p. C.*, 1912, **78**, 86; Woitaschewsky, *ibid.*, 110; Jauch, *Z. P.*, 1921, **4**, 441.

(2) Allow solvent to enter until 1 mol of solute has dissolved in the cylinder: work done $= (P + \delta P)V + (p + \delta p)\Delta v$, where $P + \delta P =$ osmotic pressure under total pressure $p + \delta p$.

(3) Decrease the external pressure to p: work done $= + \delta A$.

(4) Express from the cylinder the solvent which entered in operation (2): work done $= - PV - p\Delta v$. The cycle is complete, ∴ from (44):

$$V\delta P + \Delta v \,.\, \delta p = 0.$$

But
$$V = 1/c, \text{ and } \delta P = (\partial P/\partial c)_T \delta c$$

$$\therefore \quad V\delta P = (\partial P/\partial c)_T \delta \ln c = - \delta p \,.\, \Delta v$$

$$\therefore \quad (\partial \ln c/\partial p)_T = - \Delta v/(\partial P/\partial c)_T = - \Delta v/RT \quad . \quad . \quad [271]$$

since $P = cRT$.[1] The sign shows that if there is increase in total volume on solution, the solubility is diminished by increase of pressure, and *vice versa*. Both results have been confirmed experimentally, although the changes are small. If the solute is ionised, $P = icRT$, and, for a binary electrolyte $ca^2/(1 - a) = K$ (§ 91)

$$\therefore \quad \left(\frac{\partial \ln c}{\partial p}\right)_T = - \frac{\Delta v}{RT} \cdot \frac{2 - a}{2} \quad . \quad . \quad . \quad . \quad . \quad [272]$$

97. Gibbs's Phase Rule.—The conditions of equilibrium of a system of phases are defined in a very general manner by an equation deduced by J. Willard Gibbs.[2] The system is defined by the *number of phases*, r, the *number of components*, n (*i.e.*, the *least* number of independently variable constituents required to define the composition of all phases); the temperature; and the pressure. The influences of surface tension, electrification, and forces other than uniform pressure, are excluded from consideration in the present deduction.[3]

The assumption is made that it is possible to have a state of equilibrium between several phases at a definite temperature and pressure; this will be characterised by certain definite relations between the compositions of the phases (for example, a solid salt, saturated solution, vapour of the solvent).

For each pair of phases there must be some condition satisfied for each component, such that this particular component does not pass from one phase to the other. The r-phases may now be arranged in $(r-1)$ pairs, namely, (1, 2), (2, 3), (3, 4), .. $\{(r-1), r\}$, and there will therefore be $(r-1)$ conditions to be satisfied for each component in all the phases, that is, $(r-1)$ equations defining the equilibrium. It is evident that such pairs as (1, 3), (2, 4), etc., need not be considered, since, if phase (1) is in equilibrium with phase (2), and phase (2) with phase (3), then (1) will also be in equilibrium with (3). If this were not the case, we could, by enclosing (1), (2), (3) in a ring-shaped tube (Fig. 33), so that there are three surfaces of separation, set up a continuous circulation at a uniform temperature, which is contrary to the second law of thermodynamics.

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[1] Guldberg, 1870, Ostwald's *Klassiker*, No. 139, p. 62; Braun, *A. P.*, 1887, **30**, 250; Stackelberg, *Z. p. C.*, 1896, **20**, 337; 1898, **26**, 533; Sill, *J. A. C. S.*, 1916, **38**, 2632; Cohen and Moesveld, *Z. p. C.*, 1919, **93**, 385; Hoenen, *A. A.*, 1920, **22**, 531.

[2] *Scientific Papers*, vol. 1, pp. 62—100.

[3] J. R. Partington, *P. C. S.*, 1911, **27**, 13.

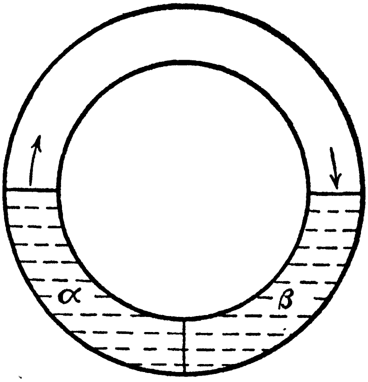

FIG. 33.

For all the components there will therefore be $n(r-1)$ equations. The number of variables is made up of:

(i.) the pressure p,

(ii.) the temperature θ,

(iii.) the number of concentrations $= r(n-1)$, since for each phase we have $(n-1)$ fractions of the total mass for the n components. The last (nth) fraction, being obtained by subtracting the sum of all the others from the total mass, is fixed, and is not an independent variable. Therefore:

$$\text{number of variables} = 2 + r(n-1).$$

The number of variables left undetermined

$$\begin{aligned} &= \text{number of variables} - \text{number of equations} \\ &= 2 + r(n-1) - n(r-1) \\ &= 2 + n - r. \end{aligned}$$

This, however, is defined as the *number of degrees of freedom* (F) of the system, hence:

$$\boldsymbol{F + r = n + 2} \quad . \quad . \quad . \quad . \quad . \quad \textbf{(273)}$$

If any component is absent from a particular phase (for example, the vapour phase, or a solid phase), there is one variable less, but also one boundary condition less, for migration of that component cannot occur with respect to the phase considered. The equation (273) is therefore still true.

Equation (273) is known as the *Phase Rule*, and finds very extensive application.

98. The Triple Point.—The Phase Rule (273) shows that the three phases, solid, liquid, and vapour, of a pure substance coexist in equilibrium only at one definite temperature and pressure. The corresponding point on the p,T diagram is known as the *triple point.*

If the volumes of liquid and solid phases are neglected in comparison with v, that of the gaseous phase, (81) and the corresponding formula for sublimation, give, for the slopes of the evaporation and sublimation curves at the triple point : $dp_e/d\mathrm{T} = \mathrm{L}_e/\mathrm{T}v$ and $dp_s/d\mathrm{T} = \mathrm{L}_s/\mathrm{T}v$.

Hence, since $\mathrm{L}_s - \mathrm{L}_e = \mathrm{L}_f$, the latent heat of fusion (see § 57) :

$$dp_s/d\mathrm{T} - dp_e/d\mathrm{T} = \mathrm{L}_f/\mathrm{T}v \quad . \quad . \quad . \quad . \quad . \quad (274)$$

The two curves meet at a finite angle, $\tan^{-1}(\mathrm{L}_f/\mathrm{T}v)$, at the triple point. Equation (274) is due to Lord Kelvin (1854).[1] Regnault, in 1847, considered that the vapour pressure of a supercooled liquid was the same as that of the solid at the same temperature, but (274) shows that this cannot be the case. The angle is usually very small.

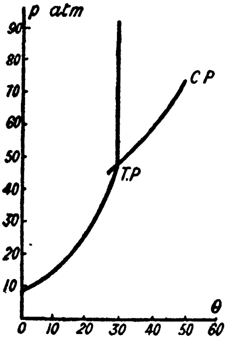

FIG. 34.

In the case of water Fischer (1886) found a difference of slope of the two curves amounting to 0·0465 mm. Hg per 1° C. The calculated difference (taking the temperature of the triple point 0° C. instead of 0·0077° C., the actual value) is ($v = 206{\cdot}6$ litres per gm.) :

$$\frac{dp_s}{d\mathrm{T}} - \frac{dp_e}{d\mathrm{T}} = \frac{80 \times 0{\cdot}0413}{273 \times 206{\cdot}6} =$$
$$0{\cdot}0000585 \text{ atm.}/1° \text{ C.} = 0{\cdot}0446 \text{ mm.}/1° \text{ C.}$$

The sublimation and evaporation curves of phosphonium chloride meet at a very decided angle at the triple point, as is seen from Fig. 34, which also shows the fusion curve and the critical point.

99. Liquid Mixtures : Duhem - Margules Equation. — The vapour in equilibrium with a homogeneous mixture of two volatile liquids has, in general, a different composition from the liquid,

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[1] *Tr. R. Soc. Edin.*, 1857, **21**, 123 (read in 1854) ; also Kirchhoff, *A. P.*, 1858, **103**, 206 ; P. Saurel, *J. P. C.*, 1902, **6**, 399 ; Duhem, *Z. p. C.*, 1891, **8**, 367 ; Roozeboom, " Heterogen. Gleichgewichte," vol. 1, 1901 ; Partington, " Thermodynamics," 1913, p. 214 ff. Variation of triple point with pressure : Porter, *P.M.*, 1915, **29**, 143.

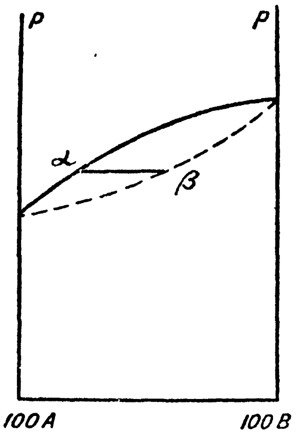

FIG. 35.

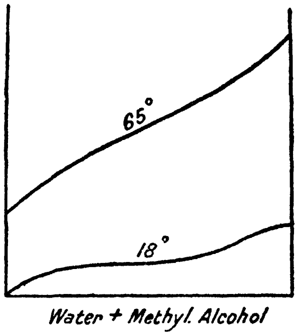

FIG. 36.

which makes it possible to separate such mixtures by distillation. The compositions of liquid and vapour, and the vapour pressures at a given temperature, may be represented by two curves, as shown in Fig. 35, in which α and β refer to liquid and vapour respectively. The constituent B has a higher vapour pressure than A, and since the vapour will be richer in this constituent than the liquid, the lower curve will correspond with vapour.

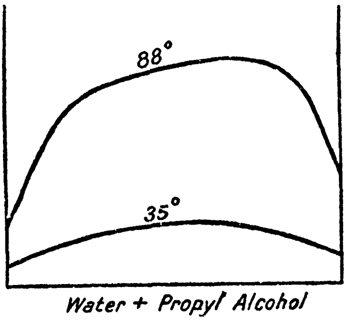

FIG. 37.

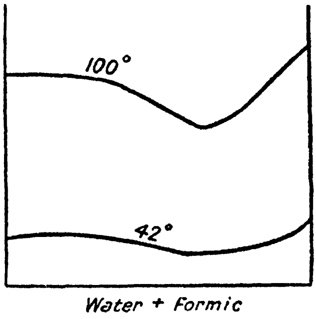

FIG. 38.

The total pressure curves of binary mixtures were experimentally investigated by Konovaloff, in 1881; the theory had previously (unknown to Konovaloff) been investigated by Gibbs, in 1875. Three cases are known, shown in Figs. 36, 37, and 38, in which the total pressure: (i.) lies between the vapour pressures of the pure constituents; (ii.) exhibits a maximum; and (iii.) exhibits a minimnm, respectively. In some cases curves of the first type show a point of inflexion, as in Fig. 36 at 18°. The total pressure curves are made up additively of the partial pressure curves of the constituents in the vapour.

The pressure changes during distillation of a binary mixture are regulated by an important rule, deduced by Gibbs, and used by Konovaloff as a consequence of some experiments of Plücker (1854), who found that the vapour pressure over a given quantity of a mixture of alcohol and water is less the larger the space which the vapour has to saturate. The *Gibbs-Konovaloff rule* may be stated as follows: During isothermal increase in volume of a vapour standing in equilibrium with a liquid mixture, the total vapour pressure either decreases or remains unchanged. When the pressure remains unchanged it is either a maximum or minimum pressure and corresponds with the case when the vapour has the same composition as the liquid.

Let N_1 mols of the first liquid (*e.g.*, alcohol), with the vapour pressure p_1^0 at the temperature T, and N_2 mols of the second liquid (*e.g.*, water), with the vapour pressure p_2^0 at the same temperature, be taken. When they are mixed together let the *partial pressures* of the two components in the vapour of the mixture be p_1 and p_2.

The mixing may be carried out isothermally and reversibly. Assume that the vapours are ideal gases, and that the volume of liquid is negligible in comparison with that of vapour.

(1) Evaporate N_1 mols of liquid (1) and N_2 mols of liquid (2) under their vapour pressures. The work done is $p_1^0v_1^0 + p_2^0v_2^0 = (N_1 + N_2)RT$.

(2) Expand the vapours to the partial pressures p_1 and p_2. The work done is:

$$RT(N_1 \ln p_1^0/p_1 + N_2 \ln p_2^0/p_2).$$

(3) Condense the two vapours through semipermeable partitions on the liquid mixture in such a way that the composition of the latter remains constant. The work done is

$$-(p_1v_1 + p_2v_2) = -(N_1 + N_2)RT.$$

The total work done is:

$$A = RT(N_1 \ln p_1{}^0/p_1 + N_2 \ln p_2{}^0/p_2) \quad . \quad . \quad . \quad [275]$$

The work done when a small quantity δN_1 mols of liquid (1) is transferred isothermally and reversibly from pure liquid to a large quantity of solution is $\delta A = \delta N_1 \,.\, RT \ln p_1{}^0/p_1$.

Hence $\qquad \partial A/\partial N_1 = RT \ln p_1{}^0/p_1$.

Let $x = N_1/(N_1 + N_2)$, then $1 - x = N_2/(N_1 + N_2)$, where x and $1 - x$ are the *molar fractions* of (1) and (2) in the liquid mixture

$$\therefore \qquad dN_1 = N_2 dx/(1 - x)^2 \quad (N_2 \text{ const.})$$

$$\therefore \qquad \left(\frac{\partial A}{\partial x}\right)_{N_2} = \frac{RTN_2}{(1-x)^2} \ln \frac{p_1{}^0}{p_1} \quad . \quad . \quad . \quad . \quad . \quad [276]$$

Differentiate [275] with respect to x (N_2 const.) and compare with [276], then:

$$x(\partial \ln p_1/\partial x) + (1 - x)(\partial \ln p_2/\partial x) = 0 \quad . \quad . \quad . \quad (277)$$

This is the equation deduced by Duhem and integrated by Margules.[1]

The differential equation (277) contains two dependent variables, p_1 and p_2, and is therefore indeterminate. The only condition imposed is that each side of the equation must be a symmetric function of x and $1 - x$. The integration assumed by Margules and simplified by Porter is:

$$p_1 = p_1{}^0 x e^{\beta(1-x)^2}$$

$$p_2 = p_2{}^0(1 - x)e^{\beta x^2}$$

which satisfies the differential equation, β being a constant.

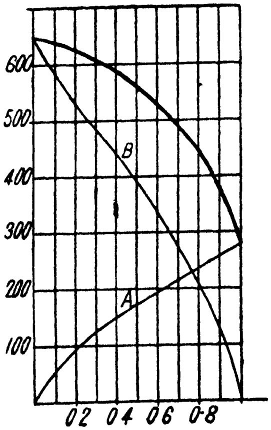

FIG. 39.

The equations may be applied in constructing the partial pressure curves of mixtures, *e.g.*, of acetone and ethyl ether (Fig. 39). In this case a value of $\beta = 0{\cdot}7414$ at 30° (the only arbitrary constant involved) was found to reproduce the partial pressure curves. At 20°, $\beta = 0{\cdot}75$. The abscissæ represent molar fractions of acetone, and the ordinates pressures in mm. Hg. The thick line is the total pressure curve; A, B are the partial pressure curves of acetone and ether.

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[1] A. W. Porter, *F. S.*, 1920, **16**, 336; 1922, **17**, 19; Duhem, *C. R.*, 1886, **102**, 1449; "Mécan. chim.," t. III., ch. 7 (1899); Margules, *W. B.*, 1895, **104**. ii., 1243; E. Bose, *Z. p. C.*, 1909, **65**, 458; Rosanoff, *J. A. C. S.*, 1914, **36**, 1408; Rosanoff and Easley, *Z. p. C.*, 1910, **68**, 641; Story, *ibid.*, **71**, 129; Plank, *P. Z.* 1910, **11**, 49; Konovaloff, *A. P.*, 1881, **14**, 34, 219; *J. C. P.* 1907, **5**, **1**, 237; Wrewsky, *Z. p. C.*, 1912, **81**, 1; *ibid.*, 1913, **83**, 551; F. H. Campbell, *F. S.*, 1915, **11**, 91; Rosanoff, Bacon and Schulze, *J. A. C. S.* 1914, **36**, 1993.

The curves for mixtures of ether and sulphuric acid cannot be represented by any value of β, and in this case chemical action probably occurs.[1]

Differentiate [275] with respect to T and use (197). The *heat of admixture* (evolved) [2] is then:

$$U_1 - U_2 = Q(N_1, N_2, T)$$
$$= -RT^2 . \partial/\partial T[N_1 \ln (p_1{}^0/p_1) + N_2 \ln (p_2{}^0/p_2)] . \quad [278]$$

which is a generalisation of Kirchhoff's equation [267].

The *critical temperature*, T_c of a mixture of liquids can be obtained approximately from those of its components by the mixture rule [3]:

$$T_c = (m_1 T_{c_1} + m_2 T_{c2})/(m_1 + m_2).$$

The following formula connecting the *density* of a pure liquid $1/v_\theta$ with the temperature θ was put forward by Avenarius [4]: $v_\theta = a - b \log (\theta_c - \theta)$, where a and b are constants. According to Herz,[5] this formula also holds for mixtures of liquids. Thorpe and Rücker [6] give an alternative formula: $\theta_c = (Tv_\theta - 273)/2(v_\theta - 1)$. Mendeléeff gives the relation $\rho_\theta = \rho_0 (1 - K\theta)$.[7]

100. Heat of Evaporation.—In comparing the heat of evaporation of a binary liquid mixture with those of the pure components, we may first consider the mixture resolved into these, with *absorption* of heat Q, the heat of admixture, and then each pure liquid evaporated with absorption of its latent heat. If the liquid contains N_1 mols of (1) and N_2 mols of (2), the heats absorbed in the separation of 1 mol of (1) and (2), respectively, are dQ/dN_1 and dQ/dN_2. If λ_1, λ_2 are the heats of evaporation of 1 mol of (1) and of (2), respectively, from the mixture, and λ_1', λ_2' the latent heats of evaporation of the pure liquids:

$$\lambda_1 = \lambda_1' + dQ/dN_1 \quad \text{and} \quad \lambda_2 = \lambda_2' + dQ/dN_2.$$

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[1] For a discussion of the various types of curves, see Ostwald's "Lehrbuch der allgemeinen Chemie," II., **2**, (1), 612–648. On partially miscible liquids, *ibid.*, 687 ff.

[2] Heats of admixture, see Linebarger, *P. R.*, 1896, **13**, 418.

[3] Strauss and Pawlewski, *B.*, 1882, **15**, 460, 2460. See also Winkelmann. "Handbuch der Physik," 1906, Vol. III., p. 850; Centnerszwer, *Z. p. C.*, 1906, **54**, 689; Schulze, *P. Z.*, 1912, **13**, 425; Campetti, *Atti. R. Acad. Sci. Torino*, 1913, **48**, 968.

[4] *Petersburg Acad.*, 1877, **10**, 697.

[5] *Z. an. C.*, 1918, **104**, 251.

[6] *C. S.*, 1884, **45**, 135.

[7] See Herz, *Z. p. C.*, 1913, **85**, 632; *ibid.*, 1914, **87**, 63; von Jüptner, *Z. p. C.*, 1910, **73**, 173.

From [82] we thus find :

$$\left.\begin{aligned}\lambda_1 - dQ/dN_1 &= RT^2 . d \ln p_1{}^0/dT\\ \lambda_2 - dQ/dN_2 &= RT^2 . d \ln p_2{}^0/dT\end{aligned}\right\} \quad . \; . \; . \quad [279]$$

where $p_1{}^0$, $p_2{}^0$ are the vapour pressures of the pure liquids.[1]

By considering the evaporation of 1 mol of each constituent, under its partial pressure, from a large mass of liquid mixture, we find :

$$(\partial p_1/\partial T)_x = p_1\lambda_1/RT^2 \text{ and } (\partial p_2/\partial T)_x = p_2\lambda_2/RT^2 \quad . \quad [280]$$

$$\left.\begin{aligned}\partial \ln (p_1/p_1{}^0)_x/\partial T &= (\partial Q/\partial N_1)_T/RT^2\\ \partial \ln (p_2/p_2{}^0)_x/\partial T &= (\partial Q/\partial N_2)_T/RT^2\end{aligned}\right\} \quad . \; . \; . \; . \quad [281]$$

giving a relation between the partial pressures, the vapour pressures, and the heat of admixture as a function of composition and temperature.

If we put $\qquad Q = (N_1 + N_2)q \quad . \; . \; . \; . \; . \; . \; . \quad (282)$

we find, since $N_1/(N_1 + N_2) = x$:

$$\left.\begin{aligned}(\partial Q/\partial N_1)_T &= q + (1 - x) . \partial q/\partial x\\ \text{and} \qquad (\partial Q/\partial N_2)_T &= q - x . \partial q/\partial x\end{aligned}\right\} \quad . \; . \; . \; . \quad (283)$$

From [281] and (283) we find :

$$q + (1 - x)(\partial q/\partial x)_T = RT^2 . \partial/\partial T \,[\ln (p_1/p_1{}^0)]_x$$

$$q - x(\partial q/\partial x)_T = RT^2 . \partial/\partial T \,[\ln (p_2/p_2{}^0)]_x$$

$$\therefore \quad q = RT^2 . \partial/\partial T[x \ln (p_1/p_1{}^0) + (1 - x) \ln (p_2/p_2{}^0)]_x \quad . \quad [284]$$

$$(\partial q/\partial x)_T = RT^2 . \partial/\partial T \,[\ln (p_1/p_1{}^0) - \ln (p_2/p_2{}^0)]_x \quad . \; . \; . \; . \quad [285]$$

due to Nernst,[2] and Ostwald,[3] respectively.

EXAMPLES XIV.

1. Show that the temperature coefficient of the degree of ionisation of a univalent electrolyte, $1/\alpha . d\alpha/dT$, is equal to $Q_V(1 - \alpha)/RT^2(2 - \alpha)$. Find the value of this for a 0·05 molar solution of acetic acid at 18° C., given the dilution law constant $K = \alpha^2/(1 - \alpha)v = 0{\cdot}0_4180$ (v in litres), and Q_V = 28 cal.

2. The values of $K_W = C_{H^{\cdot}} \times C_{OH'}$, the dissociation constant of water at 0° C. and 50° C., are $0{\cdot}09 \times 10^{-14}$ and $4{\cdot}5 \times 10^{-14}$. Calculate the heat of ionisation at 25° C.

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[1] Ostwald, "Lehrbuch," II., ii., 646 (1911); R. Gahl, *Z. p. C.*, 1900, **33**, 178; Zawidzki, *ibid.*, 1900, **35**, 128 (partial pressures).

[2] "Lehrbuch," 1 Aufl., 1893; 8–10 Aufl., p. 122, equation (2).

[3] "Lehrbuch," II., ii., p. 647 (1911); cf. Duhem, "Mécanique chim.," t. IV., 15 ff.

3. The figures given below were found by Nernst (1891) when studying the partition of phenol between water and benzene :

c_1 (conc. in H_2O) .	0·051	0·123	0·327	0·75 mols/lit.
c_2 (conc. in C_6H_6) .	0·077	0·159	0·253	0·39 „

Calculate the constants according to the equation $c_2^2/c_1 = k$ and interpret the results.

4. The solubility of I_2 in water is 0·03004 gm. per 100 gms. of solution at 25° C. ; the solubility in CCl_4 at the same temperature is 30·33 gms. per litre. The distribution ratio of I_2 between these liquids is 85·3. Calculate the concentration of the I_2 in water if, after shaking with CCl_4, the concentration in the latter is 10·88 mols/litre.

5. Nernst found the following figures in an experiment on the partition of CH_3COOH between water and C_6H_6 (c_1 = conc. of acid in H_2O ; c_2 = conc. in C_6H_6) :

$c_1 = 0·043$	0·071	0·094	0·149
$c_2 = 0·245$	0·314	0·375	0·500

Given that the partition coefficient is of the form $c_2^m/c_1^n = k$, find the values of m, n and k and say what you know about the state of acetic acid in solution.

6. At 25° C. the distribution coefficient of bromine between CCl_4 and water is 38. The partial pressure of Br_2 above a 0·05 molar solution in water at 25° C. is 50 mm. If 1 litre of this solution is shaken with 50 c.c. of CCl_4 what will be the pressure of the bromine over the CCl_4 phase ? (Assume the partial pressure of the Br_2 to be proportional to the molar fraction in the solution.)

7. The partition coefficient of I_2 between water and amyl alcohol is 230 at 25° C. (= c_1/c_2, where c_1 = mols of I_2 per litre of alcohol and c_2 = mols of I_2 per litre of water). One litre of water is shaken with 400 c.c. $C_5H_{11}OH$ containing 1 gm. I_2 per litre. Calculate the weight of I_2 which enters the aqueous layer.

8. Find the partition coefficient of $C_6H_5.COOH$ between H_2O and C_6H_6 :

c_1 (conc. in H_2O) .	0·0150	0·0195	0·0289	gms. per 10 c.c.
c_2 (conc. in C_6H_6) .	0·242	0·412	0·970	

By plotting c_1^2 against c_2 show that the partition coefficient is given by the tangent of the angle of slope of the graph at any point.

9. The integral heat of solution of 1 mol K_2SO_4 in 100 mols water at 15° C. is 6580 cals. (Berthelot). The heat evolved when this solution is diluted by the addition of 400 mols water is 248 cals. Find the heat of solution of 1 mol K_2SO_4 in 400 mols water at 15° C.

10. The specific heats of mixtures of 1 mol H_2SO_4 with 5 and 10 mols H_2O are 0·545 and 0·700. Find the change in the heat of dilution of the first solution to the second with 1° C. in temperature.

11. Solutions of TlCl saturated at 25° C. and 39·7° C. contain 0·386 and 0·604 per cent. Assuming a mean ionisation of 90 per cent., find the heat of solution of 1 mol.

12. If *Q* is the heat of dilution per mol of solvent, assumed independent of temperature, show by integration of Kirchhoff's equation (38a), and the combination of the result of Examples IX., No. 8, with the equation for osmotic pressure : $P = RT \ln (p_0/p)$ that :

(i.) at the freezing point T′ of the solution :

$$P = \Delta t\left[\frac{\lambda_0^f}{T_0} - \frac{C_l - C_s}{2}\frac{\Delta t}{T'} + \frac{C_l - C_s}{3}\frac{(\Delta t)^2}{T^{2\prime}}\right]$$

(ii.) at any temperature T

$$P = \Delta t\left[\frac{\lambda_0^f + Q}{T} - \frac{C_l - C_s}{2}\frac{\Delta t\,.\,T_0}{T^2} + \frac{C_l - C_s}{3}\frac{(\Delta t)^2 T_0}{T^3}\right]$$

where Δt = depression of freezing point; C_l, C_s are the molecular heats of liquid and solid solvent; λ_0^f is the latent heat of fusion at 0°K; T_0 = freezing point of pure solvent.

13. The heat of solution at 18° C. of *a* gm. water and *b* gm. $NaNO_3$ is given by $23{\cdot}061\, b\,(b + 0{\cdot}8791\, a)/(b + 0{\cdot}3261\, a)$ absorbed. The solution is saturated when $b/a = 0{\cdot}8665$. Find the heat of solution of 1 gm. water and 0·8665 gm. $NaNO_3$. Find $d \log(p_0/p)/dT$. Find the heat absorbed when 1 gm. of water is added to an infinite amount of saturated solution and thence calculate $\partial \log(p/p_0)/\partial T$ at concentration 0·8665.

14. The integral heat of solution of HI in water, Q_X, is a cubical function of m, the percentage of water in the mixture (Bose). Thomsen found the figures given below for the intergal heat of solution of HI in water at 17° C. :

$x = \frac{\text{mol } H_2O}{\text{mol HI}}$.	Q_x at 17° C.	$x = \frac{\text{mol } H_2O}{\text{mol HI}}$	Q_x at 17° C.
2	12,540 g. cals.	20	18,990 g. cals.
3	14,810 ,,	50	19,140 ,,
5	17,380 ,,	100	19,180 ,,
10	18,580 ,,	500	19,210 ,,

Find the relation between Q_X and m ; thence find an expression for the differential heat of dilution, Q_d, in terms of m.

15. If P is the vapour pressure of pure water at the absolute temperature T, and p is that of a saturated aqueous salt solution, then $T \ln (P/p)$ is a linear function of temperature (Speranski, 1912). Given that $d \ln P/dT = Q/RT^2$ for pure water, Q being the heat of vaporisation of 1 mol of water, show that l, the integral heat of solution of a saturated salt solution in 1 mol of water, is a constant.

16. The solubility of NaCl in water at 24·05° C. is given by the equation $c = 35{\cdot}898 + 0{\cdot}001647\, p - 0{\cdot}0_63286 p^2$, where c is in gms. per 100 gms. H_2O, and p is the pressure in atmospheres. Calculate the volume change when 1 mol of salt is dissolved in a litre of water under a pressure of 1 atm. (Density of water at 24·05° C. = 0·99732.)

17. A function $\phi(x_1, x_2, \ldots x_n)$ of *n* variables is said to be *homogeneous* and of the *m*th degree when the equation $k^m \phi(x_1, x_2, \ldots x_n) = \phi(kx_1, kx_2, \ldots kx_n)$ is true for all values of *k* and the variables. Show that :

$$x_1 \,.\, \partial\phi/\partial x_1 + x_2 \,.\, \partial\phi/\partial x_2 + \ldots = m\phi \text{ (Euler's theorem).}$$

Thence show that, if Z is the thermodynamic potential of a solution :

$$Z = m_1\mu_1 + m_2\mu_2 + \ldots$$

where, $m_1, m_2, \ldots$ are the masses of the components and $\mu_1, \mu_2, \ldots$ their chemical potentials.

Also

$$m_1 \,.\, \partial\mu_1/\partial m_1 + m_2 \,.\, \partial\mu_1/\partial m_2 + \ldots = 0$$
$$m_1 \,.\, \partial\mu_2/\partial m_1 + m_2 \,.\, \partial\mu_2/\partial m_2 + \ldots = 0$$
$$\partial\mu_2/\partial m_1 = \partial\mu_1/\partial m_2, \text{ etc.}$$
$$m_1 \,.\, \partial\mu_1/\partial m_1 + m_2 \,.\, \partial\mu_2/\partial m_1 + \ldots = 0$$
$$m_1 \,.\, \partial\mu_1/\partial m_2 + m_2 \,.\, \partial\mu_2/\partial m_2 + \ldots = 0.$$

In the case of a binary mixture :

$$m_1 \,.\, \partial\mu_1/\partial m_1 + m_2 \,.\, \partial\mu_1/\partial m_2 = m_1 \,.\, \partial\mu_1/\partial m_1 + m_2\partial\mu_2/\partial m_1 = m_1 \,.\, \partial\mu_1/\partial m_2 + m_2 \,.\, \partial\mu_2/\partial m_2,$$

and if $m_2/m_1 = s$, $\partial\mu_1/\partial s + s \,.\, \partial\mu_2/\partial s = 0.$

18. Show that if an equilibrium constant is defined for the reaction $n_1A_1 + n_2A_2 + \ldots \rightleftarrows n_1'A_1' + n_2'A_2' + \ldots$ in the form $\Sigma n_1 \ln \bar{c}_1 = \ln \bar{K}$, where $\bar{c}_1 = n_1/\Sigma n_1$, then $(\partial \ln \bar{K}/\partial p)_T = -\Delta v/RT$, for a mixture of ideal gases or a dilute solution, where Δv is the total *increase* in volume of the system when the above reaction takes place (Planck). If K is the ordinary equilibrium constant, $\ln K = \Sigma n_1 \ln (n_1/V)$, show that $(\partial \ln K/\partial p)_T = -\Delta v/RT - \Sigma n_1/V \cdot \partial V/\partial p$.[1]

19. Show that if *c* is the solubility of a gas in a liquid, in mols per litre, $(\partial \ln c/\partial T) = Q_V/RT^2$, where Q_V is the heat absorbed per mol of gas dissolving in a large volume of saturated solution.

20. Show that the prolongation of the vapour pressure curve of a liquid below the freezing point (metastable region) lies *above* the vapour pressure curve of the solid form. Also that the prolongation of any curve beyond a triple point must lie between the other two curves which meet at that point.

21. Show that, in a system of two phases in equilibrium, the only possible spontaneous transition which can occur just above/(below) the saturation curve $p = f(T)$ is one which leads to diminution/(increase) of volume when it occurs on the saturation curve (G. Robin).

22. Show that the only possible spontaneous transition which can occur in the region to the right/(left) of the saturation curve is one which leads to absorption/(emission) of heat when it occurs on the saturation curve. (Moutier).

23. Show that the following relations hold for the three curves meeting in a triple point (s = entropy):

$$(v_2 - v_3) \cdot dp_1/dT + (v_3 - v_1) \cdot dp_2/dT + (v_1 - v_2) \cdot dp_3/dT = 0$$
$$(s_2 - s_3) \cdot dT/dp_1 + (s_3 - s_1) \cdot dT/dp_2 + (s_1 - s_2) \cdot dT/dp_3 = 0.$$

Thence show, that if an isotherm $T \pm dT$ is drawn to cut the three curves of transition (or their prolongations) meeting at a triple point, the central point of section corresponds with the transition involving the greatest change of volume (Moutier, 1876). Also that if an isobar $p \pm dp$ is drawn to cut the three curves of transition (or their prolongations), the central point of section corresponds with the transition involving the greatest change of entropy (Roozeboom, 1901).

24. The triple point divides each curve passing through it into two parts, one corresponding with a stable, and the other with an unstable, system. If there is a reversible change which increases the entropy of the system but leaves its volume unchanged, and another reversible change which increases the volume but leaves the entropy unchanged, there will, in each case, be an increase in the amounts of some phases at the expense of the others. Show that if the mass of any phase decreases the system from which it is absent cannot exist in stable equilibrium at temperatures and pressures lower than those corresponding with the triple point (Roozeboom, 1887).

25. Show that the system of two phases corresponding with the transition involving the greatest change in volume is in stable equilibrium at temperatures which lie on one side of the triple point, while the other two systems are in stable equilibrium at temperatures which lie on the opposite side (Duhem, 1891).

26. The system of two phases which corresponds with the greatest change of entropy is in stable equilibrium under pressures lying on one side of the triple point, while the other two systems are in stable equilibrium under pressures lying on the other side (Roozeboom, 1901).

27. If a small circuit is drawn round the triple point, it cuts alternately

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[1] Rice, *F. S.*, 1917, **12**, 318; cf. Porter, *ibid.*, 1920, **15**, 75.

stable and unstable branches of the transition curves meeting at that point (Gibbs, 1876).

28. Dolezalek applied the Duhem-Margules equation: $d \ln p_1/dx + x \,.\, d \ln p_2/dx = 0$ to aqueous hydrochloric acid on the assumption that $-\ln p_1 (H_2O) = a \ln x + k$, where a and k are constants. The agreement was fairly satisfactory from $p_2 = 0{\cdot}52$ to 277 mm.[1] Lapworth, Lingford and Jones,[2] in the case of alcoholic hydrogen chloride, put $d \ln p_1/dx = a' + b'x + d'x^2 \therefore \ln p_2 = a_0 \ln x + b_0 x + d_0 x^2 + k_0$, or, with numerical constants: $\log 10p_2 = 1{\cdot}284 \log X + 0{\cdot}01106\, X + 0{\cdot}0_3 115 X^2 - 0{\cdot}256$, where $X = 100\, x$. Calculate the values of p_2 for $x = 0{\cdot}1965$, $0{\cdot}0696$, and $0{\cdot}0162$, and compare with the observed values 4·69, 0·811, and 0·108.

29. In a solution containing $n_1, n_2, \ldots$ mols of different solvents, with vapour pressures $p_1^0, p_2^0, \ldots$ to 1 mol of solute, show that $n_1 \ln (p_1^0/p_1) + n_2 \ln (p_2^0/p_2) + \ldots = 1$, where $p_1, p_2, \ldots$ are the pressures after addition of solute.[3] If p, P are the vapour pressures of solvent and of a *volatile* solute, thence show that $d \ln p/dx + x \,.\, d \ln P/dx = 0$, where x = molar fraction of solute.

30. In a mixture of benzene and carbon disulphide between temperatures of 48°—77° C. the molar fractions of benzene in the liquid (x_1) and vapour (y_1) are given by $(1 - y_1)/y_1 = 3{\cdot}32[(1 - x_1)/x_1]^{0{\cdot}9}$. Find the composition of the distillates from mixtures containing 90% and 10% of benzene.

31. In the case of mixtures of two immiscible liquids, the composition of the vapour is independent of the proportions of the components, provided large enough quantities of the latter are present. The vapour pressures of C_6H_5Cl and H_2O are[4]:

t = 90° C.	... C_6H_5Cl :	208·35 mm.	... H_2O :	525·45 mm.
91° C.	...	215·8 ,,	...	545·8 ,,
92° C.	...	223·45 ,,	...	566·75 ,,

Calculate the percentages of C_6H_5Cl in the vapour by weight at the three temperatures.

32. If m_a' and m_b' are the relative masses of two infinitely miscible liquid substances a and b in the vapour over a liquid mixture of the substances in the proportions m_a and m_b, then according to Brown (1881) $m_a' \,.\, m_b = c \,.\, m_a \,.\, m_b'$, where $c = P_a/P_b$, the ratio of the vapour pressures of the two substances.

The following figures relate to a mixture of CCl_4 and CS_2:

% CCl_4 (mols) in liq.		c.		B P. (750 mm.).		Obs. % CCl_4 (in vap.).
20	...	0·3649	...	49·0° C.	...	9·4
40	...	0·3726	...	53·2	...	19·6
50	...	0·3771	...	55·8	...	25·8
60	...	0·3825	...	59·0	...	33·8
80	...	0·3947	...	66·5	...	57·6

Calculate the percentage composition of the vapour at the B.P. for each mixture.

33. Lehfeldt has modified the Duhem-Margules expression to the formula $t = Kq^r$, where t = ratio of the masses of the two substances in the vapour, q = ratio in the liquid, K = const. and $r = (\log s - \log p_a/p_b)/\log (Bq/A)$ where p_a and p_b are the vapour pressures of the pure liquids at the temperature of the experiment, s = ratio of the number of molecules of the two

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[1] *D. p. G.*, 1903, **5**, 4.

[2] *C. S.*, 1913, **103**, 260.

[3] Nernst, *Z. p. C.*, 1893, **11**, 1.

[4] Young, "Distillation Principles and Processes," 1922, p. 78.

substances in the vapour ; A and B are the normal molecular weights of the components.

For a mixture of C_6H_6 and CCl_4, r = 0·947 and log K = 0·065. Test the relation for mixtures of these liquids containing the following molecular percentages of C_6H_6 in the liquid : 17·0, 34·0, 62·4, 80·3, 95·7. [The observed percentages of C_6H_6 in the vapour for these concentrations are : 16·5, 32·3, 58·8, 76·7, 94·6.] Show also that a mixture of minimum B.P. would contain 5·6% C_6H_6 by weight.

34. The vapour pressure of benzene at 34·8° C. = 14·54 cm. Hg and that of chlorobenzene at the same temperature = 2·03 cm. Calculate :

(i.) The partial pressure of benzene in a mixture of 58·28 gms. chlorobenzene and 66·16 gms. benzene.

(ii.) The partial pressure of chlorobenzene in a mixture of 28·39 gms. of benzene and 61·78 gms. chlorobenzene.

(iii.) The partial pressures of both chlorobenzene and benzene in a mixture of 73·19 gms. of the former with 27·25 gms. of the latter.

(Assume the partial pressures of the constituents are proportional to the molar fractions of the latter in the liquid and also the Guthrie formula of Ex. 42.)

35. Show that the ratio of the weights of the components of a mixture of two immiscible liquids distilling over is $p_1{}^0m_1 : p_2{}^0m_2$, where m = molecular weight. A mixture of water and $C_6H_5NO_2$ boils at 99° C. at 1 atm. pressure. Assuming the liquids to be immiscible find the vapour pressure of $C_6H_5NO_2$ at 99° and the composition of the distillate. (Assume ideal gases ; vapour pressure of water at 99° = 733 mm.)

36. In the case of a mixture of chlorobenzene and bromobenzene the partial pressure of each constituent is proportional to the molar fraction in the liquid. The vapour pressures at 140° C. are : C_6H_5Cl 938·8 mm. ; C_6H_5Br 496·7 mm. What mixture boils at 140° under a pressure of 760 mm. ? Find the molar fractions of chlorobenzene and bromobenzene in the vapour from mixtures containing (*a*) 1% C_6H_5Cl ; (*b*) 1% C_6H_5Br. What is the composition of the liquid when the partial pressures of the two constituents are equal ?

37. Mixtures of benzene and ethylene dibromide behave like those in the question above. At 50° C. the vapour pressures are : C_6H_6 269·0 mm., $C_2H_4Br_2$ 43 mm. What is the molar fraction of benzene in the vapour when that in the liquid is 0·5, and *vice-versâ ?*

38. In the case of mixtures of ethyl alcohol and ether the molar fraction in the vapour is related to that in the liquid by the formula $p_1 = x_1(p_1{}^0)^n$, where n is a constant. At 10° C. the vapour pressures of the pure liquids (p_0) are : ether 291·8 mm., alcohol 23·8 mm. If n = 0·5, draw the total vapour pressure curve of mixtures of the two liquids and by means of the curve find the composition of the mixture of maximum vapour pressure.

39. Schilow and Lepin (1922) found the following figures for the distribution of salicylic acid between benzene and water at 25° C. :

C_1 = Conc. in mol/lit. in water layer.	C_2 = Conc. in mol/lit. in benzene layer.	C_1/C_2.
0·0363	0·0184	1·97
0·0668	0·0504	1·32
0·094	0·0977	0·96
0·126	0·146	0·86
0·210	0·329	0·64
0·283	0·533	0·53
0·558	1·650	0·34
0·756	2·810	0·27
0·912	4·340	0·21

Obviously the relation $C_1/C_2 = const.$ does not hold. Find the distribution equation for this system, on the assumption it is of the form $C_1/C_2{}^n = const.$ (Plot log C_1 against log C_2; find n from the slope of the line and the constant from the intercept on the log C_1 axis.)

40. 100 c.c. C_6H_5Cl and 80 c.c. water were distilled together, the atmospheric pressure being 740·2 mm. The B.P. was found to be somewhere between 90–91° C. The vapour pressures of C_6H_5Cl and of water are 208·35 mm. and 525·45 mm. respectively at 90°, and 215·8 mm. and 545·8 mm. at 91°. Calculate the true B.P. of the mixture. [Assume dp/dT to be constant over the range of 1°.]

41. Rosanoff (1914) has put forward the following formula connecting the vapour pressure P of mixtures of CCl_4 (a) and C_6H_6 (b) at 49·99° C. with m (= % of component a):

$$P = 268{\cdot}075 + 80{\cdot}853\ m. - 43{\cdot}826\ m^2 + 16{\cdot}531\ m^3 - 13{\cdot}695\ m^4.$$

Find the composition of the mixture of maximum vapour pressure at 49·99° C., and find the value of the latter.

Given, also, that $(\log_{10} P_a - \log_{10} P_b)/(P_a - P_b) = 0{\cdot}0015103$ at 49·99° C. for the mixture $CCl_4 + C_6H_6$, calculate P for mixtures of the following concentrations:

Molec. % CCl_4 in liquid: 5·07, 11·70, 17·58, 25·15, 29·47, 39·53, 55·87, 67·55, 76·52.
P (obs.) mm.: 271·8, 277·6, 281·5, 285·4, 288·3, 294·5, 301·0, 305·2, 306·8.

42. Guthrie (1884) put forward the following formula for the vapour pressure P of a mixture of two liquids, a and b of vapour pressures P_a and P_b respectively (P, P_a and P_b being measured at the same temperature): $100P = mP_a + (100 - m)P_b$, m being the percentage by weight of the liquid a. This formula only holds if the liquids a and b show no volume or heat change on mixing. Speyers (1900) showed that m is more accurately represented by the molecular percentage of a, provided the critical pressures of a and b are nearly equal.

Test the equation from the following figures for a mixture of C_6H_5Br and C_6H_5Cl:

m (C_6H_5Br)=25·01.	Pa=452·85 mm.	Pb=862·95 mm.	at B.P.=136·75° C.
50·00.	526·25 „	992·30 „	142·16° C.
73·64.	618·40 „	1153·00 „	148·16° C.

The observed value for P in each case is, of course, 760 mm.

43. The following table gives P_b, the vapour pressure of C_6H_5Cl in mm. and P_a the vapour pressure of C_6H_5Br in mm. at various temperatures t (° C.):

t.	P_b.	P_a.	t.	P_b.	P_a.
132	760·25	395·1	144	1039·5	553·2
134	802·15	418·6	146	1092·9	583·85
136	845·85	443·2	148	1148·4	615·75
138	891·4	468·9	150	1206·0	649·05
140	938·85	495·8	152	1265·8	683·8
142	988·2	523·9	154	1327·9	719·95
			156	1392·3	757·55

Assuming the Speyers-Guthrie formula (question 42) plot m against the temperature and find the boiling point of the mixture when m = 50·00 and the molecular percentage of C_6H_5Br in a mixture boiling at 148·16° C. (both at a pressure of 760 mm.)

CHAPTER XV

Capillarity and Adsorption

101. Surface Tension.—The surface of a liquid behaves as though it were an elastic skin tightly stretched. If an attempt were made to increase the surface by pulling upon an imaginary line 1 cm. in length, located in the surface, at right angles to this line in the plane of the surface, the force opposing such an increase of surface is called the *surface tension* σ (often called γ) of the liquid. If the line is displaced 1 cm., the free energy of the surface will be increased by σ, so that the surface tension per unit length is numerically equal to the *surface energy* per unit area. The surface tends to become as small as possible under given conditions.[1] The dimensions of surface tension are *force/length = energy/area.*

Experiments show that there is a definite surface energy located in the interface between *any* two phases (solid, liquid, gas): its amount will be denoted generally by σ per unit area. This is the *free energy* of the surface.[2]

102. Effect of Surface Tension on Vapour Pressure.—The vapour pressure of a liquid in the form of drops, or otherwise exhibiting a curved surface, is different from that over a plane liquid surface (Lord Kelvin, 1870).[3]

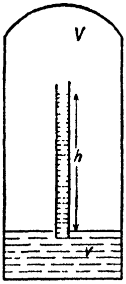

FIG. 40.

In Fig. 40 the liquid is supposed to wet the glass and ascend in the capillary tube to the height h, with a concave meniscus exposed to the vapour. The hydrostatic pressure in the *liquid* just below the concave surface of the meniscus in the tube is less than that just beneath the plane surface in the vessel by the amount $hg\rho = hg/v$, where ρ is the density, and v thespecific volume, of the liquid. The pressure in the vapour similarly differs by hg/V, where V is the specific volume of the vapour. If π, π' are the hydrostatic pressures in the liquid, and p, p' the vapour pressures :

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[1] See Poynting and Thomson's "Properties of Matter," chap. 14; Ferguson, *F. S.*, 1922, **17**, 370 ff.

[2] For surface tension and molecular attraction, cf. Harkins and Grafton, *J. A. C. S.*, 1920, **42**, 2534; Harkins and Ewing, *ibid.*, 2539; Harkins and Cheng, *J. A. C. S.*, 1921, **43**, 35; Harkins and Feldman, *ibid.*, 1922, **44**, 2665.

[3] *P. M.*, 1871, **42**, 448; A. Bacon, *P. R.*, 1905, **20**, 1.

$$p - p' = \delta p = hg/V$$

$$\pi - \pi' = \delta\pi = hg/v$$

$$\therefore \quad \delta p = \delta\pi \, . \, v/V \quad . \quad . \quad . \quad . \quad . \quad . \quad (286)$$

giving the change of vapour pressure when the pressure on the liquid itself is changed in any way by an amount $\delta\pi$ (say by pumping an indifferent gas into a vessel [illegible] liquid in equilibrium with vapour).[1]

The *increase* in vapour pressure of water at 0° C. per 1 atm. will be v/V atm. $= 18/22{,}400$ approximately $= 0{\cdot}0008$ atm. $= 0{\cdot}61$ mm., the vapour pressure of water being then 4·6 mm. (15 per cent.). At 70° C. the effect is 0·15 mm. on a vapour pressure of 149·5 mm. (0·1 per cent.). The relative change diminishes rapidly with increase of temperature.

The vapour pressure of *small drops* of water is greater than that over a plane surface (see formula 287 below). For a radius of 10^{-4} cm. the increase is about 1 in 1000; for $r = 10^{-6}$ cm. the increase is 10 per cent., and for 10^{-7} cm., 100 per cent. For very small drops, however, the surface tension may diminish.

Experiment shows that instead of this small increase in vapour pressure there is a larger diminution of vapour pressure of a liquid when the measurements are made in the presence of an inert gas. The cause is unknown.[2]

If we combine (286) with the simple formula for the ascent of liquids in capillary tubes (spherical meniscus) :

$$\sigma = \tfrac{1}{2} rhg/v \quad \text{or} \quad h = 2\sigma v/rg$$

we find

$$\delta p = p - p' = 2\sigma v/rV \quad . \quad . \quad . \quad . \quad . \quad (287)$$

and

$$\delta\pi = \pi - \pi' = 2\sigma/r \quad . \quad . \quad . \quad . \quad . \quad . \quad (288)$$

(287) gives the excess of vapour pressure of a spherical drop of radius r over the vapour pressure of a plane surface ; (288) gives the excess of hydrostatic pressure inside the drop over that outside.

The above formulæ are approximate, since the density of vapour throughout the column h is assumed uniform. A more exact formula may be obtained by supposing a small mass δm of liquid transferred from a drop of radius r_1 to a drop of radius r_2. The work done by the surface forces $= \sigma \times$ *decrease in surface.*

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[1] Gibbs, " Scientific Papers," I., 160 ; cf. Niggli, *Z. an. C.*, 1915, **91**, 107 ; Wegscheider, *ibid.*, 1915, **93**, 95. Poynting, *P. M.*, 1881, **12**, 32 ; J. J. Thomson, " Applications of Dynamics to Physics and Chemistry," 1888, p. 168 ; Le Chatelier, *Z. p. C.*, 1892, **9**, 335 ; Schiller, *A. P.*, 1894, **53**, 396 ; 1907, **60**, 755.

[2] Cf. Partington and Huntingford, *C. S.*, 1923, **123**, 161. For the surface tensions of liquids in contact with different gases, see Ferguson, *P. M.*, 1914, **28**, 403.

Let δv, δr, δa be the changes in volume, radius, and surface of one drop due to the change of mass δm. Then $\delta v = \delta m/\rho = v\delta m$. But $\delta v = \delta(4/3 . \pi r^3) = 4\pi r^2 \delta r$, and $\delta a = \delta(4\pi r^2) = 8\pi r \delta r$ $\therefore \quad \delta a = 2v\delta m/r$

$$\therefore \quad \text{decrease of surface} = 2v\delta m(1/r_1 - 1/r_2)$$

$$\therefore \quad \text{work done} = 2\sigma v(1/r_1 - 1/r_2)\delta m = A_1.$$

If δm is returned by isothermal distillation, the work done is [154]:

$$\delta m(RT/M) \ln (p_2/p_1) = A_2$$

where M = mol. wt. of *vapour.*

The cycle is now complete $\therefore A_1 + A_2 = 0$

$$\therefore \quad (RT/M) \ln (p_2/p_1) = 2\sigma v(1/r_2 - 1/r_1)$$

or

$$\ln \frac{p_2}{p_1} = \frac{2\sigma v M}{RT} \left(\frac{1}{r_2} - \frac{1}{r_1}\right) \quad . \quad . \quad . \quad . \quad . \quad [289]$$

If we put $V = RT/Mp$ in (287) and $r_2 = r$, $r_1 = \infty$ (plane surface), and assume that $p_2 - p_1 = p - p'$ is small, equation [289] goes over into (287).

In osmotic equilibrium the *vapour* pressures of solution and water under the pressures π' and π (§ 53) must be equal. If p_0, p_1 are the vapour pressures of pure water and solution, equation (286) shows that: $\ln (p_0/p_1) = M_1 P v_1/RT$, where P is the osmotic pressure $= \pi' - \pi$, M_1 is the molar weight of the solvent vapour, and v_1 is the increase in volume of a large amount of solution when 1 gm. of solvent is added. If ρ is the density of a solution containing N_1 mols solvent and N_2 mols solute in V litres, and $c = N_2/V$ = molar concentration of solute, then $1000\rho V = N_1M_1 + N_2M_2$. Also $M_1v_1 = (\partial V/\partial N_1)_{N_2}$ $\therefore$ (since $dV = -V/c . dc$) $1/M_1v_1 = 1000\,(\rho - c . d\rho/dc)/M_1$. The equation for P then becomes:

$$P = \frac{1000\,RT}{M_1}\left(\rho - c\frac{d\rho}{dc}\right) \ln \frac{p_0}{p_1}$$

which was used by Lord Berkeley and Hartley[1] in calculating results of osmotic pressures of $Ca_2FeC_6N_6$ in water at 0° C.

Gms. in 1000 gm. H_2O.	ρ.	c.	$d\rho/dc$.	p_0/p_1 obs.	P calc. atm.	P obs. atm.
313·9	1·224	1·001	0·202	1·033	41·27	41·22
428·9	1·287	1·323	0·188	1·070	87·35	87·09
499·7	1·322	1·509	0·180	1·107	132·8	130·66

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[1] *P. T.*, 1906, **206**, 481.

If $\rho - c \, . \, d\rho/dc = \text{const.} = \rho_0$, we recover the simple equation [155], which reproduces the above results with an error not exceeding 5 per cent.

Effect of surface tension on melting point.—Pawloff[1] found that with crystals of salol with surfaces lying between 228—1296 μ^2 ($\mu = 10^{-3}$ mm.) the melting point decreases 2·8° C. per 100 times increase of surface.

103. Effect of Surface Tension on Solubility.—The effect of surface tension on solubility may be calculated in a way similar to that used in deducing [289]. If P_1, P_2 are the *osmotic* pressures of solutions in equilibrium with spherical particles of solute of radii r_1 and r_2:

$$\ln \frac{P_2}{P_1} = \ln \frac{c_2}{c_1} = \frac{2\sigma v M}{RT}\left(\frac{1}{r_2} - \frac{1}{r_1}\right)$$

where v is the specific volume of the solid and M its molar weight *in solution.*[2] If $r_1 \rightarrow \infty$, the excess solubility of a substance in spherical particles of radius r over that of large pieces ($r \rightarrow \infty$) is given by

$$\ln (c_r/c_\infty) = 2\sigma v M/RTr \quad . \quad . \quad . \quad . \quad . \quad [290]$$

If the solute is ionised, and the degree of ionisation is assumed constant over the range of dilution involved, then (cf. § 75):

$$i \ln (c_r/c_\infty) = 2\sigma v M/RT.$$

In the case of gypsum, $\sigma = 1050$ erg/cm^2. at 25° C., $v = 1/2{\cdot}33$, $R = 8{\cdot}316 \times 10^7$ erg/1°, $M = 136(CaSO_4)$, $i = 1{\cdot}65$, hence

$$\log c_r = \log c_\infty + 0{\cdot}00040/Tr.$$

At 0° C. the solubility of large crystals is 12·93 *mgm. mols/litre;* that of particles of radius 0·001 mm. will then be 13·37 *mgm. mols/litre.*[3]

104. Theory of Supersaturation.—The above considerations throw some light on the phenomena exhibited by supersaturated solutions (cf. references to § 103). These are caused to crystallise by the introduction of a particle of the solid only when the latter exceeds a certain size.[4] Smaller particles dissolve, and [290] shows that there is one particular size of particle which is in equilibrium with a supersaturated solution of given concentration.

By comparing [290] with [211], which may be written:

$$\ln c_\infty = -\frac{\lambda_0}{RT} + \frac{a}{R} \ln T + k$$

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[1] *Z. p. C.*, 1910, **74**, 562.

[2] Hulett, *Z. p. C.*, 1901, **37**, 385; 1904, **47**, 357; W. J. Jones, *Z. p. C.*, 1913, **82**, 448; *A. P.*, 1913, **41**, 441; W. J. Jones and J. R. Partington, *P. M.*, 1915, **29**, 35; M. Jones and J. R. Partington, *C. S.*, 1915, **107**, 1019; Freundlich, "Kapillarchemie," 1922, p. 207; Dundon and Mack, *J. A. C. S.*, 1923, **45**, 2479.

[3] Solubility of different faces of a crystal: J. Lebrun, *Bull. Acad. Roy. Belg.*, 1913, p. 953; Ritzel, *Z. p. C.*, 1913, **86**, 106.

[4] Ostwald, *Z. p. C.*, 1897, **22**, 289; "Lehrbuch," II., 2, i., 704 ff. (bibliography).

as is seen when $\lambda = \lambda_0 + a\mathrm{T}$ is substituted in [208], where $\lambda_0 =$ heat of solution at the absolute zero, and a is a constant, we find :

$$c_r = \mathrm{A}e^{\left\{\frac{2\mathrm{M}\sigma}{\mathrm{RT}\rho r} - \frac{\lambda_0}{\mathrm{RT}} + \frac{a}{\mathrm{R}}\ln \mathrm{T} + k\right\}}.$$

By comparing this with the corresponding equation for the temperature $\mathrm{T} + d\mathrm{T}$ we find on making use of the experimental fact (293) that $d\sigma/\sigma = d\rho/\rho$, approximately, that :

$$-d\mathrm{T}\left\{\frac{1}{\mathrm{T}} - \frac{k'r}{\mathrm{T}} - k_1 r\right\} - \frac{dr}{r} = 0,$$

where $k' = \lambda_0\rho/2\mathrm{M}\sigma$, and $k_1 = a\rho/2\mathrm{M}\sigma$.

Now λ_0 is large compared with a, so that k_1 may be neglected in comparison with k', and the above equation on integration then gives :

$$\mathrm{T} = \mathrm{T}_\infty(1 - 1/k'r) \quad . \quad . \quad . \quad . \quad . \quad . \quad [291]$$

where T_∞ is the value of T for $r \rightarrow \infty$, *i.e.*, the temperature corresponding with saturation of a solution in contact with large pieces of solid which has the same concentration as the supersaturated solution (in equilibrium with particles of radius r) at the temperature T.

If $\lambda_0 > 0$, *i.e.*, heat is absorbed when solid passes into solution, and hence, by [211] the solubility increases with rise of temperature, $1 - 1/k'r < 1$. With diminishing r, equation [291] shows that T then decreases. The tendency to spontaneous formation of a particle of sufficient size to bring about precipitation, by molecular collisions, will become more and more probable as the temperature is lowered, first on account of the fact deduced from the above equation that a smaller particle is then sufficient, and second, because the number of molecules with small kinetic energies is then larger. The number of centres causing spontaneous crystallisation will therefore increase rapidly with fall in temperature, as is actually the case.[1]

When $\lambda_0 < 0$, *i.e.*, heat is evolved when solid passes into solution, and the solubility diminishes with rise of temperature, then $1 - 1/k'r > 1$, *i.e.*, the temperature of supersaturation increases as the particles diminish in size. In this case lowering of temperature favours the formation of clusters by molecular collision, as before, but it also retards precipitation, which then requires larger particles. A solution of calcium butyrate saturated at 18° C.

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[1] Jaffé, *Z. p. C.*, 1903, 43, 565 ; Miers and Isaac, *C. S.*, 1906, 89, 413.

first deposits crystals (under a layer of paraffin oil) when heated to 42° C.[1]

105. Latent Heat of Extension of a Surface.—Consider a surface film of area a, exhibiting the surface tension σ at temperature T. Let the following cycle be carried out:

(1) Increase the a to $a + da$ at constant T. The work done is:

$$\delta A_1 = -\sigma da \quad (da > 0).$$

(2) Lower the temperature to $T - dT$ at constant area:

$$\sigma \text{ changes to } \sigma - (d\sigma/dT)dT.$$

(3) Allow the film to contract to the original area. The work done is $\delta A_2 = [\sigma - (d\sigma/dT)dT]da \quad (da < 0).$

(4) Raise the temperature of the film to T.

The cycle is now complete; the total work done

$$= (\delta A) = \delta A_1 + \delta A_2 = -(d\sigma/dT)dTda.$$

If l_a = heat absorbed per unit increase of surface at constant temperature = *latent heat of extension,* then (46) gives:

$$l_a = -T(d\sigma/dT) \quad . \quad . \quad . \quad . \quad . \quad . \quad (292)$$

which is analogous to (47) and is due to Lord Kelvin.[2]

In all cases (for a pure liquid or a solution) σ *decreases* with rise of temperature, approximately linearly:

$$\sigma_\theta = \sigma_0(1 - \gamma\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (293)$$

The coefficient γ is *approximately* equal to the rate of decrease of density with the temperature[3]:

$$\rho_\theta = \rho_0(1 - \gamma\theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad (294)$$

(292) shows that a surface film *absorbs* heat on extension. In the case of water at room temperature $d\sigma/dT = -1/7$ approx., $\therefore -T \cdot d\sigma/dT = 290/7 = 41 = \sigma/2$ approx. (σ for water $= 76$); the latent heat of extension in this case is equal to about half the work spent in producing the extension.

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[1] Jones and Partington, *C. S.*, 1915, **107**, 1019; Freundlich, "Kapillarchemie," 2nd ed., 1922, pp. 440 ff.

[2] *P. R. S.*, 1858, **9**, 255; *P. M.*, 1859, **17**, 61.

[3] A more accurate relation in the neighbourhood of the critical point T_c is given by van der Waals:

$$\sigma = A(1 - T/T_c)^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (293a)$$

where A is a constant independent of temperature. At $T = T_c$ both σ and $d\sigma/dT$ are zero, in agreement with experiment. Instead of 3/2, the exponent 1·23 gives better results.

MacLeod (*F. S.*, 1923, **19**, 38) uses the equation $\sigma/(\rho_l - \rho_v)^4 = const.$, where ρl and ρ_v are the densities of the liquid and vapour. Ferguson (*F. S.*, 1923, **19**, 407) has proposed an equation of which MacLeod's is a special case.

According to Ferguson (*P. M.*, 1916, **31**, 37), the power law $\sigma = \sigma_0(1 - b\theta)^n$ where b is approximately $1/\theta_c$, is usually quite satisfactory. Cf. R. Swinne, *Z. p C.*, 1912, **79**, 461.

The *intrinsic energy* per unit surface, u_a, is given by equation (201):

$$u_a = \sigma - \mathrm{T} \, . \, d\sigma/d\mathrm{T} \quad . \quad . \quad . \quad . \quad . \quad (295)$$

in which σ has the significance of a *free energy* per unit surface.[1]

The *molar free surface energy* is the surface energy associated with 1 mol (M gm.) of liquid in the form of a sphere:

$$\mathrm{F}_a = 4{\cdot}836\sigma\,(\mathrm{M}v)^{\frac{2}{3}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (296)$$

where v is the specific volume. It was found by Ramsay and Shields [2] that the dependence on temperature is given by:

$$\sigma(\mathrm{M}v)^{\frac{2}{3}} = k\,(\mathrm{T}_c - \mathrm{T} - \tau) \quad . \quad . \quad . \quad . \quad . \quad (297)$$

where τ is a small correction (*c.* 6°) which must be subtracted from T_c in order that the σ, T curve shall remain a straight line to the point of intersection with the T axis.

Richards and Matthews[3] give the following relation between η_θ, the isothermal compressibility, and σ for a liquid: $\eta_\theta\sigma^{4/3} = \text{const.} = 0{\cdot}00253$ for pressures between 100 and 500 atm. Tyrer[4] finds that, to 1 atm. $\eta_\theta\sigma^{4/3} = \sqrt[3]{\mathrm{T}} \times \text{const.}$; the "constant" varies from $1{\cdot}026 \times 10^{-3}$ to $1{\cdot}52 \times 10^{-3}$. Amagat[5] has deduced the equation

$$\eta_\theta = \mathrm{T} \, . \left(\frac{dv}{d\mathrm{T}}\right)_p . \, v/\text{const.}$$

The value of k in (297), which should be independent of the nature of the liquid, is obtained from the equation:

$$k = \{\sigma_1(\mathrm{M}v_1)^{\frac{2}{3}} - \sigma_2(\mathrm{M}v_2)^{\frac{2}{3}}\}/(\mathrm{T}_2 - \mathrm{T}_1) \quad . \quad . \quad (298)$$

where σ_1, v_1, and σ_2, v_2 are the values at T_1 and T_2 respectively.

For a large number of non-associated liquids of not too high molecular weight k has the value 2·12. Liquids known to be associated (*e.g.*, alcohols, water, acids) give smaller values of k, variable with temperature, and this is assumed to mean that the normal value of M, taken in (298), is too small.[1] Fused salts give a very small value of k (0·6), practically independent of temperature. With substances of high molecular weight (*e.g.*, fats such as tristearin), k may reach the value 5.[2]

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[1] Bennett and Mitchell, *Z. p. C.*, 1913, **84**, 475. Whittaker (*P. R. S.*, 1908, **81**, 21) suggests that $u_a = \left(\frac{\mathrm{K}}{\mathrm{M}}\right)\mathrm{TL}i$, where $\mathrm{L}i$ is the internal latent heat (see § 40), M = mol. wt.

Kleeman (*P. M.*, 1909, **18**, 39) suggests that $\mathrm{K} = 0{\cdot}557\ \mathrm{M}^{\frac{1}{3}}\rho_c{}^{\frac{2}{3}}/\mathrm{T}_c$. Kleeman (*P. M.*, 1909, **18**, 491, 901) finds that at corresponding states the values of u_a/σ, the ratio of surface tensions of different liquids, $\mathrm{L}_i\mathrm{M}^{\frac{1}{3}}\rho^{\frac{2}{3}}/\sigma$, $\mathrm{L}_i{}^{\frac{1}{3}}\mathrm{M}^{\frac{7}{6}}/\rho^{\frac{2}{3}}$, and $\mathrm{L}_i\rho/p_c$, are constant.

Hammick (*P. M.*, 1921, **41**, 21; *ibid.*, 1919, **38**, 240) deduces $1/\eta = -2\mathrm{L}_{i\rho}$ (η = compressibility) if a in van der Waals' equation is independent of volume. If a depends on volume: $1/\eta = \frac{v}{\sigma} \cdot \frac{d\sigma}{d\mathrm{T}} \cdot \frac{d\mathrm{T}}{dv} . \mathrm{L}_i\rho$.

[2] *P. T.*, 1893, **184**, 647.

[3] *Z. p. C.*, 1908, **61**, 449.

[4] *Z. p. C.*, 1914, **87**, 182.

[5] *A. C. P.*, 1877, **11**, 520.

The heat absorbed when 1 gm. of a liquid of density ρ is transferred from a drop of radius r to a plane surface is readily shown from [289] to be

$$Q = -\frac{2}{\rho r} T \frac{d\sigma}{dT} \cdot \quad . \quad . \quad . \quad . \quad . \quad (299)$$

106. Adsorption.—When two homogeneous masses are in contact at a surface of separation there is usually a change in concentration from that in the bulk of the phase to a different value at the interface. Gases tend to adhere to solid surfaces (*e.g.*, ammonia gas to charcoal), and dissolved substances tend to accumulate from solutions at such interfaces (cf. the decolorising action of animal charcoal). This is a result of the tendency of the free surface energy to become as small as possible; where this depends on the concentration, such a change of concentration will occur at the interface as will reduce the interfacial surface energy.

A change of concentration at an interface is known as *adsorption*; it is positive when the solute increases in concentration at the interface, and negative when it decreases. Both cases are observed.[3]

107. Gibbs's Adsorption Equation.—Suppose we have a solution separated from another phase with which it does not mix. Let the free surface energy per unit surface = σ. Let n_s be the *difference* between the concentration at the surface and that in the interior of the solution. Then for an infinitesimal increase in the area of the surface we have the relation (§ 90) :

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[1] Ramsay, *P. R. S.*, 1894, **56**, 171; Ramsay and Aston, *Z. p. C.*, 1894, **15**, 98; Guye and Baud, *ibid.*, 1903, **42**, 379; Grunmach, *A. P.*, 1904, **15**, 401; Bolle and Guye, *J. C. P.*, 1905, **3**, 38; Brandt, *A. P.*, 1903, **10**, 783; Nernst, "Lehrbuch," 8–10 Aufl., 316; J. L. R. Morgan, *J. A. C. S.*, 1909, **31**, 309; 1911, **33**, 643; Morgan and Cann, *ibid.*, p. 1060. Morgan puts $\sigma (Mv)^{\frac{2}{3}} = A + Bt + Ct^2$, where $B = 2C(t_c - 6)$. See also D. Tyrer, *Z. p. C.*, 1912, **80**, 50; *J. P. C.*, 1915, **19**, 81; Walden and Swinne, *Z. p. C.*, 1912, **79**, 700; 1913, **82**, 271; P. Bogdan, *ibid.*, 1913, **82**, 93.

[2] Freundlich, "Kapillarchemie," pp. 45 ff.; van der Waals, *Z. p. C.*, 1894, **13**, 657; also van der Waals, "Thermodynamik," I., 218 ff.; Prud'homme, *J. C. P.*, 1916, **14**, 285; Mathews, *J. P. C.*, 1916, **20**, 554; Jaeger and Kahn, *A. A.*, 1916, **18**, 617; *Z. an. C.*, 1917, **101**, 1.

[3] Cf. (negative adsorption) A. M. Williams, *M. K. N.*, 1913, No. 27; *F. S.*, 1914, **10**, 155, 166; Freundlich, "Kapillarchemie."

$$dz = \sigma \, . \, da + \mu \, . \, dn_s$$

where μ is the chemical potential of the solute ; dz is the increase of thermodynamic potential and must be a perfect differential. Hence $(d\sigma/dn_s)_a = (d\mu/da)_{n_s}$.

In (29) (cf. *H. M.*, § 55) :

$$(dp/dv)_\theta \, . \, (d\theta/dp)_v = - \, (d\theta/dv)_p$$

which is a general relation between the three variables p, v, θ, we can let $p = \mu$, $v = a$ and $\theta = n_s$:

$$\therefore \qquad (d\mu/da)_{n_s}(dn_s/d\mu)_a = - \, (dn_s/da)_\mu .$$

Substitute for $(d\mu/da)_{n_s}$ the expression found above :

$$\therefore \qquad (d\sigma/dn_s)_a(dn_s/d\mu)_a = (d\mu/da)_{n_s}(dn_s/d\mu)_a$$

or

$$(d\sigma/d\mu)_a = - \, (dn_s/da)_\mu \quad . \quad . \quad . \quad . \quad . \quad (300)$$

But, from [259] $\bar{\mu} = \mathrm{RT} \ln c + \mathrm{G(T)}$, or $\mathrm{d}\bar{\mu} = \mathrm{RT} \, . \, dc/c$

$$\therefore \quad \frac{c}{\mathrm{RT}}\left(\frac{d\sigma}{dc}\right)_a = - \left(\frac{dn_s}{d\alpha}\right)_\mu = - \, \Gamma \quad . \quad . \quad . \quad [301]$$

where Γ is the *adsorption excess* at unit surface, and n_s is the adsorption excess, both in *mols*.

Equation (300) was deduced by Gibbs in 1874.[1] It indicates that *a substance will tend to be adsorbed at an interface when it lowers the interfacial tension* $(\partial\sigma/\partial c < 0)$.

The equation has been tested in the case of an *air/solution* interface by Donnan and Barker [2] (1911), who passed bubbles of air through a tube containing aqueous solutions of nonylic acid or saponine. Each bubble carried with it a very slight alteration of concentration, and after a time the concentrations at the top and bottom of the tube were different. Γ (nonylic acid) $= 10^{-7}$ gm./cm^2. (agrees with calculated). Γ (saponine) $= 4 \times 10^{-7}$ gm./cm^2. (twice as great as calculated). Other experimenters obtained abnormal results.

Adsorption is usually represented by an empirical equation at a given temperature. Let m = mass of adsorbent (*e.g.*, charcoal), x = amount of substance adsorbed when equilibrium is attained, and c = concentration of the solution, then :

$$x/m = ac^{1/n} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (302)$$

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[1] " Scientif. Papers," I., 235 ; see also Milner, *P. M.*, 1907, **13**, 96 ; W. C. M. Lewis, *P. M.*, 1908, **15**, 499 ; 1909, **17**, 466 ; *Z. p. C.*, 1910, **73**, 129 ; Polànyi, *Z. p. C.*, 1914, **88**, 622 ; Porter, *F. S.*, 1915, **11**, 51.

[2] *P. R. S.*, 1911, **85A**, 557 ; also Patrick, *Z. p. C.*, 1914, **86**, 545.

where a, n are constants.[1] The values of $1/n$ vary only from 0·1 to 0·5 for dissolved substances (0·1 to 0·8 for gases), but a depends largely on the nature of the substances and adsorbent; on charcoal, $a = 2{\cdot}6$ for acetic acid, and 23·1 for bromine, in water. The following results were obtained with acetic acid in aqueous solution, and blood charcoal, at 25° C. ($a = 2{\cdot}606$; $1/n = 0{\cdot}425$.)

c mol./lit.	x/m millimols per gm. charcoal (obs.).	x/m calcd. by (302).
0·0181	0·467	0·474
0·0616	0·801	0·798
0·2677	1·55	1·49
0·8817	2·48	2·47
2·785	3·76	4·01

108. Effect of Electrification.

When a spherical drop of water carries an electric charge (*e.g.*, drops composing a thundercloud) this resides in the surface, and a charge of surface density k causes a hydrostatic tension $2\pi k^2$ to be exerted on every unit of surface, acting along the outward normal, and so tending to explode the drop.[2] By (286) this will cause a *diminution* of vapour pressure of:

$$p - p' = \delta\pi . v/V = -2\pi k^2 v/V \quad . \quad . \quad . \quad . \quad (303)$$

The effect is very small, since the greatest tension which can exist on an isolated conductor in air under atmospheric pressure is equal to a pressure of about 0·3 mm. of mercury, corresponding to a lowering of vapour pressure, in the case of water, of about 10^{-6} mm. of mercury.

The *increase* of vapour pressure, due to the influence of surface tension will, of course, be superposed on the effect due to the electrification of the drop.[3]

EXAMPLES XV.

1. Calculate the latent heat of extension of films of the following liquids at the given temperatures, $d\sigma/dT$ being the decrease of surface tension in ergs per cm². (Harkins and Roberts):

CCl_4, $d\sigma/dT = 0{\cdot}103$ at 140° C. C_6H_5Cl, $d\sigma/dT = 0{\cdot}088$ at 260° C.
Et_2O, $d\sigma/dT = 0{\cdot}112$ at 40° C. N_2, $d\sigma/dT = 0{\cdot}220$ at -193° C.
C_6H_6, $d\sigma/dT = 0{\cdot}100$ at 190° C. O_2, $d\sigma/dT = 0{\cdot}260$ at -195° C.

2. The following figures give the surface tensions in dynes/cm. of different liquids at the given temperatures:

CCl_4, $\sigma = 12{\cdot}22$ at 140° C. C_6H_5Cl, $\sigma = 7{\cdot}14$ at 260° C.
Et_2O, $\sigma = 14{\cdot}05$ at 40° C. N_2, $\sigma = 8{\cdot}27$ at -193° C.
C_6H_6, $\sigma = 19{\cdot}16$ at 190° C. O_2, $\sigma = 16{\cdot}25$ at -195° C.

Calculate, with the data in question 1, the intrinsic energy per unit surface in each case.

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[1] Further particulars of the subjects of this section will be found in Freundlich's excellent treatise, "Kapillarchemie," 2nd edit., Leipzig, 1922; see also Firth, *F. S.*, 1921, **16**, 434; *C. S.*, 1921, **119**, 926, and other papers.

On effect of temperature on adsorption: Freundlich, *ibid.*, pp. 156 ff., 180 (heat of adsorption); Williams, *F. S.*, 1914, **10**, 167.

[2] Cf. J. J. Thomson, "Elements of Electricity and Magnetism," 1904, § 37.

[3] See Blondlot, *J. P.*, 1884, [ii.], **3**, 442; Gouy, *C. R.*, 1909, **149**, 822. For the effect of magnetic field on solutions, see Duhem, *Ann. Ecole normale Super.*, 1890 [iii.], **7**, 289; also Koenigsberger, *A. P.*, 1898, **66**, 698. For the effect of gravity on the concentration of a solution, see Vegard, *P. M.*, 1907, **13**, 589, and Lippmann, *C. R.*, 1911, **152**, 239.

3. According to J. L. R. Morgan the molecular surface energy of ethyl alcohol is given by the expression

$$\gamma\,(Mv)^{2/3} = 347{\cdot}26 - 0{\cdot}8772\,t - 0{\cdot}002377\,t^2$$

t being in °C. Calculate the degree of association between the temperatures 0° and 20° C. (take the constant for non-associated liquids as 2·12).

4. The surface tension of PCl_3 is 28·71 dynes at 16·4° C. and 24·91 dynes at 46·2° C. The density of the liquid at these temperatures is 1·582 and 1·527. Is PCl_3 associated over this range of temperature ?

5. The surface tension of liquid hydrogen iodide is given, according to McIntosh and Steele (1909), by $29{\cdot}06\,(1 - 0{\cdot}00265T)/0{\cdot}402951$. Calculate the Ramsay and Shield's constant for this liquid over the range − 48° C. to − 37° C., given that the density is related to the temperature by the expression $d_T = 2{\cdot}799\,[1 + 0{\cdot}0043\,(237{\cdot}4 - T)\,]$.

6. The surface tension of Br_2 is given by the relation $\sigma = 42{\cdot}00\,(1 - 0{\cdot}00381\,t)$, where t is the temperature C. Is liquid Br_2 associated over the range 0° C. — 100° C ? (Take the Ramsay and Shield's constant as 2·12. The specific volume of Br_2, according to Thorpe, is given by the equation $v/v_0 = 1 + 0{\cdot}00106218\,t + 0{\cdot}0_5187\,t^2 - 0{\cdot}0_83085\,t^3$, which holds between 0° and the B.P., 63° C.)

7. The following figures were found by King and Wampler (1922) when studying the adsorption of aqueous ester solutions [Temp. = 20° C.].

	Diethyl Tartrate.		*Diethyl Malonate.*		*Diethyl Succinate.*	
	Conc. in mols per 1000 g. H_2O	σ dynes/cm.	Conc. in mols per 1000 g. H_2O.	σ dynes/cm.	Conc. in mols per 1000 g. H_2O.	σ dynes/cm.
(*a*)	0·673058	48·890	0·1344000	43·685	0·1125350	43·159
(*b*)	0·340050	53·120	0·0677000	51·115	0·0562670	51·480
(*c*)	0·170030	57·235	0·0338500	56·705	0·0281340	55·815
(*d*)	0·085010	60·860	0·0169200	61·250	0·0140670	60·283
(*e*)	0·042500	63·970	0·0084600	64·825	0·0070334	63·940
(*f*)	0·021250	66·720	0·0042300	67·700	0·0035167	66·760
(*g*)	0·010625	68·652	0·0021150	69·750	0·0017583	68·932
(*h*)	0·005312	70·150	0·0010570	70·965	0·0008791	70·453
(*k*)	0·002656	71·175	0·0005275	71·710	0·0004395	71·416
(*l*)	0·001328	71·880	0·0002637	72·115	0·0002197	71·870
	Pure water	72·6	Pure water	72·6	Pure water	72·6

Calculate Γ for each concentration, using Gibbs's adsorption equation. It is an instructive exercise to plot log (conc.) against σ.

8. The following figures relate to the adsorption of *l*-leucine by animal charcoal; a is the percentage concentration of the leucine in the solution, x is the percentage amount adsorbed.

$$x = 0{\cdot}598,\ 0{\cdot}401,\ 0{\cdot}356,\ 0{\cdot}237,\ 0{\cdot}141,\ 0{\cdot}107$$
$$a = 1{\cdot}850,\ 0{\cdot}925,\ 0{\cdot}696,\ 0{\cdot}463,\ 0{\cdot}2786,\ 0{\cdot}221.$$

Plot the adsorption isotherm (*i.e.*, plot x against $(a - x)$). Also plot log x against log $(a - x)$; this graph (allowing for experimental errors in a and x) is a straight line which changes its slope at about log $(a - x) = 3$. Calculate the constants in the adsorption isotherm $x = k\,(a - x)^{1/n}$ for each half of this graph.

9. The adsorption of glycyl *l*-leucine by animal charcoal from solution is given by the following figures:

a = percentage concentration of the acid.
x = percentage amount adsorbed.
a = 1·91, 1·0, 0·955, 0·477, 0·400, 0·318.
x = 0·744, 0·488, 0·496, 0·286, 0·235, 0·198.

Plot the curve and find the constants in the adsorption isotherm, using the method outlined in the question above.

10. The vapour pressure of ether at 0° C. is 184·9 mm. Find the vapour pressure when the pressure on the liquid is 100 atm. The specific volumes of the liquid and vapour are 1·358 c.c. and 1209 c.c.

11. The specific volume of ice at 0° is 1·092. Show that the vapour pressure increases by pressure to the extent of 0·088 % per atm.

12. If p_0, p_1 are the vapour pressures of a liquid exposed to the action of gravity at heights h_0, h_1 in the column, show that $p_0 - p_1 = g(h_1 - h_0)/V$, where g = acceleration of gravity and V = specific volume of vapour.

CHAPTER XVI

Electrochemistry

109. Single Electrode Potential.—A metal immersed in a solution of its ions tends to pass into solution as charged ions, leaving the metal negatively charged (*e.g.*, Zn in $ZnSO_4$, Aq), or ions tend to deposit from the solution giving the metal a positive charge (*e.g.*, Cu in $CuSO_4$,Aq):

$$Zn = Zn^{++} + 2\ \ominus\ ;\ Cu^{++} = Cu + 2\ \oplus.$$

The charged free ions will move up to the oppositely charged metal surface, and an *electrical double layer* will be produced.

Consider a small charge δe transported from metal to solution, in the form of $\delta e/yF$ mols of ions (y = valency of the ion; F = 1 faraday = 96,500 coulombs). The free energy of the metal decreases by $f_0\delta e/yF$, where f_0 is the free energy of the metal per mol; whilst the free energy of the solution increases by $(\delta e/yF)$. $\partial f/\partial n$, where $\partial f/\partial n$ is the increase in free energy of the solution when 1 mol of ion is added, *i.e.*, the chemical potential of the ion, $\bar{\mu}$ (§ 90). The total diminution of free energy of the system is:

$$(\delta e/yF)(f_0 - \partial f/\partial n) = (\delta e/yF)(f_0 - \bar{\mu}).$$

This is equal to the *electrical work* done, $E\delta e$, where E is the potential difference in the double layer, or the *single electrode potential*, hence, generally:

$$E\delta e + (\delta e/yF)(f_0 - \bar{\mu}) = 0$$

$$\therefore\quad -E = (f_0 - \bar{\mu})/yF \quad . \quad . \quad . \quad . \quad . \quad (304)$$

For a *dilute solution* [259] gives:

$$E = (-f_0 + \bar{\mu}_0 + RT \ln c)/yF = (-f_0 + \bar{\mu}_0)/yF + RT/yF.\ln c$$

$$\therefore\quad \mathbf{E = E_0 + RT/yF\,.\ln c} \quad . \quad . \quad . \quad . \quad . \quad \mathbf{[305]}$$

where $E_0 = (-f_0 + \bar{\mu}_0)/yF = -RT \ln C/yF$, say, is the value of E when the solution contains 1 mol of ions per litre ($c = 1\ \therefore \ln c = 0$), and is called the *electro-affinity*. The sign of the electrode potential is taken as the sign of the charge on the metal (or other) *electrode*, the potential of the normal hydrogen electrode being taken as zero.[1]

Electro-Affinities (in volts).[2]

$Li^{\cdot}$	$-3{\cdot}022$	$(H_2)H^{\cdot}$	$\pm 0{\cdot}000$
$Rb^{\cdot}$	$-2{\cdot}922$	$Cu^{\cdot\cdot}$	$+0{\cdot}34$
$K^{\cdot}$	$-2{\cdot}920$	$Hg_2^{\cdot\cdot}$	$+0{\cdot}799$
$Na^{\cdot}$	$-2{\cdot}710$	$Ag^{\cdot}$	$+0{\cdot}800$
$Mg^{\cdot\cdot}$	$-1{\cdot}55$	$O_2+2H_2O-4F=4OH'$	$+0{\cdot}397$
$Zn^{\cdot\cdot}$	$-0{\cdot}758$	I'	$+0{\cdot}54$
$Fe^{\cdot\cdot}$	$-0{\cdot}42$	Br'	$+1{\cdot}066$
$Cd^{\cdot\cdot}$	$-0{\cdot}40$	$2H_2O \rightleftharpoons O_2 + 4H^{\cdot}$	$+1{\cdot}23$
$Sn^{\cdot\cdot}$	$-0{\cdot}14$	Cl'	$+1{\cdot}36$
$Pb^{\cdot\cdot}$	$-0{\cdot}13$		

Electrode potentials are usually determined in molar *salt* solutions, but as these are generally 80 per cent. ionised, the ion concentration is 0·8 molar, and the correction to 1·0 molar is only 0·006 volt.[3]

110. Alternative Deduction of the Electrode Potential Equation.

The following deduction is based on the discussion of Nernst.[4] It is assumed that a metal in a liquid tends to throw off ions in virtue of a *solution pressure*, P. The ions in the liquid, on the other hand, tend to redeposit on the metal, in virtue of their *osmotic pressure*, p. At a certain concentration of the ions, C, the osmotic pressure balances the solution pressure, and there is equilibrium. The charge acquired by the metal will depend on the relative values of P and p. When $P > p$, ions will be thrown off, and the metal will acquire a negative charge. When $P < p$, ions will deposit, and the metal will acquire a positive charge. Let us consider the second case in detail.

When the metal is immersed in a solution of concentration $c > C$ of its ions, the latter will be driven out of solution on to the metal, and will give the latter a positive charge, setting up a potential difference between the metal and solution, the magnitude of which is, say, E.

Now, suppose a small mass of metal passes into solution as ions. This will cause a small charge $+\delta e$ to pass from the metal to the solution. Since the metal is charged positively and the solution negatively, the motion of these ions *does* work $E\delta e$.

Owing to the small solution pressure in the case considered, the metal ions in the solution in equilibrium with the metal surface will be at a smaller concentration, C, than the concentration c in the bulk of the solution. The value of C will, since there is equilibrium, be given by $P = CRT$, where P is the solution pressure.

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[1] The temperature of the hydrogen electrode is taken as 18° C. Effect of pressure of the hydrogen is given by $\Delta E = \frac{RT}{2F} \cdot \ln \frac{p}{p'}$, giving (at *c.* 760 mm.) 0·00001746 volt/mm. (obs. 0·00001751, Acree and Loomis, *J. A. C. S.*, 1916, **38**, 2391).

[2] Macdougall, "Thermodynamics and Chemistry" (New York, 1921), p. 325; Lewis and Randall, "Thermodynamics," 1923, p. 433.

[3] Cf. F. Foerster, "Elektrochemie wässeriger Lösungen," 3rd edit., 1922; Lehfeldt, "Electrochemistry," 2nd edit., 1908; Jahn, "Elektrochemie."

[4] *Z. p. C.*, 1889, **4**, 129.

During the small change, the ions are transferred from a lower to a higher concentration, and work is therefore done against the osmotic forces. The small change is isothermal and reversible, hence by (187) the total work vanishes.

The osmotic work per mol is given (§ 90), since the ions are transferred from a solution of concentration C to one of concentration c, by:

$$-RT \, . \ln c \text{ (final conc.)}/C \text{ (initial conc.)}.$$

Thus, if δn mols are transferred:

$$E \, . \, \delta e + \delta n \, . \, RT \ln \frac{c}{C} = 0.$$

Thus, since $\delta e = \delta n \, . \, yF$, where F is the charge per gm. equiv., and y is the valency of the ion:

$$E = -\frac{RT}{yF} \ln \frac{C}{c} = -\frac{RT}{yF} \ln \frac{P}{p} \quad . \ . \ . \ . \ . \ . \quad [306]$$

In this formula the value of R must be in joules/1° = 8·315, when E is in volts and F in coulombs: 1 volt × 1 coulomb = 1 joule. We also change from ln to log, by dividing by 0·4343, and find:

$$E = -\frac{8{\cdot}316 \times T}{0{\cdot}4343 \times 96{,}500 \times y} \log \frac{P}{p} = -\frac{0{\cdot}0002T}{y} \log \frac{P}{p}{}^{1}$$

$$\therefore \qquad \mathbf{E = -\frac{0{\cdot}0002T}{\mathit{y}} \log \frac{C}{\mathit{c}}} \quad . \ . \ . \quad \mathbf{[306a]}$$

If we put $c = 1$, we find:

$$E_0 = -\frac{0{\cdot}0002T}{y} \log C \quad . \ . \ . \ . \ . \quad [306b]$$

which is the *electro-affinity*, and is characteristic of each metal, since P, which corresponds with C, is the solution pressure. Thus:

$$\mathbf{E = E_0 + \frac{0{\cdot}0002T}{\mathit{y}} \log \mathit{c}} \quad . \ . \ . \quad \mathbf{[306c]}$$

which enables us to calculate the electrode potential for any concentration from the value of the electro-affinity E_0 given in the table in § 109.

If E_1 and E_2 are the electrode potentials of two metals (or other ionising conductors) in solutions of their ions, the E.M.F. of the cell formed when the solutions are put in conducting contact is $E_1 - E_2$, provided contact potential differences between the solutions are eliminated.

The values of the electro-affinities given in the table are calculated with reference to the normal hydrogen electrode. The

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[1] More correctly, 0·0001984 instead of 0·0002.

absolute electrode potential, *i.e.*, the difference of potential between electrode and solution, is found by adding the absolute potential of the hydrogen electrode, 0·274 volt, to these values.

The *solution pressure* is calculated from the electrode potential as follows. In the case of zinc, $E_0 = -0{\cdot}76$ volt, hence the absolute potential is $-0{\cdot}76 + 0{\cdot}274 = -0{\cdot}486$ volt. If P is the solution pressure :

$$-0{\cdot}486 = -\frac{0{\cdot}0002T}{2}\log\frac{P\text{ atm.}}{22{\cdot}4\text{ atm.}}$$

hence $P = 1{\cdot}3 \times 10^{18}$ atm. (The exponent is positive, since a solution pressure greater than P will make E negative, by convention.) Such large values are probably meaningless.[1]

111. Heat of Ionisation.—The heat evolved when 1 electrochemical equivalent of a metal is converted into its ions at a reversible electrode is called the *heat of ionisation*, *q*.

Ostwald assumes that the Gibbs-Helmholtz equation (221) applies to each electrode separately, and hence, per electrochemical equivalent :

$$E = q + TdE/dT \quad . \; . \; . \; . \; . \quad (221a)$$

Bouty has made measurements with cells of the type :

$$Cu/CuSO_4Aq\,.\,cold/CuSO_4Aq\,.\,hot/Cu,$$

and the E.M.F. then gives dE/dT directly. This was compared with the heat evolved at the electrode, the latter being composed of a thermometer coated with copper by electrolysis. If q' is the reversible heat effect at such an electrode : q' (absorbed) $= E - q = TdE/dT$.

The directly observed value of the heat absorbed by a copper electrode in copper nitrate solution per second was 0·508 ergs; the value calculated from dE/dT was 0·528 ergs. The value of dE/dT was the same in copper sulphate as in copper acetate solution, showing that the effect is independent of the anion.

The heat absorbed when 1 coulomb crosses the boundary between metal and solution is $E - q$. From (221a) we find, per *mol* of ion produced : $Q = yF(E - TdE/dT)$. In the case of copper : $y = 2$; $E = 0{\cdot}34 + 0{\cdot}274 = 0{\cdot}61$ volt ; $T\,.\,dE/dT = 0{\cdot}22$ volt/1° (obsd., $T = 290°$ K.), hence, since $2F = 2 \times 96{,}500$ coulombs, and since volt × coulomb = 0·239 cal., Q = 18,000 cal. This is the heat of ionisation (evolved): $Cu = Cu^{\cdot\cdot} + 18,000$ cal.

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[1] Cf. Lehfeldt, *P. M.*, 1901, **1**, 377.

In a similar way the value: $Zn = Zn^{\cdot\cdot} + 33,680$ cal. was found. Now consider the reactions:

$$\begin{aligned} Zn + 2H^{\cdot} + 2Cl' &= Zn^{\cdot\cdot} + H_2 + 2Cl' + 34,200 \text{ cal.} \\ Zn &= Zn^{\cdot\cdot} + 33,680 \text{ cal.} \end{aligned}$$

By subtraction we find $H_2 = 2H^{\cdot} - 520$ cal.

This value is very small, and may usually be neglected: the heat of ionisation of hydrogen is practically zero. Thus, the heat of ionisation of a metal is practically equal to its heat of solution in a strong (highly ionised) acid with evolution of hydrogen.[1]

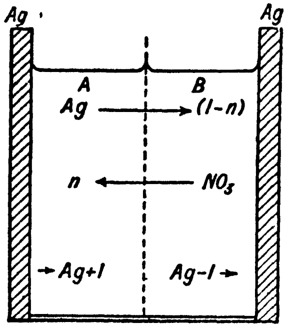

FIG. 41.

The above considerations show that the heat of precipitation of one metal from a solution of a salt by means of another metal should be independent of the anion. This result was found experimentally by Andrews in 1844.[2]

112. Concentration Cells.—A *concentration cell* is usually formed of two identical electrodes in two solutions of different concentrations, *e.g.*:

$$Ag/AgNO_3 \text{ sol. conc. } c_1/AgNO_3 \text{ sol. conc. } c_2/Ag.$$

The source of the E.M.F. is then to be sought in the tendency of the dissolved substance to equalise its concentration. When the solutions are dilute there is no heat of dilution, and as there is no heat of reaction, $q = 0$ in (221a), hence $dE/E = dT/T$, *i.e.*, the E.M.F. is proportional to the absolute temperature.

Consider the above case in detail. Silver dissolves in the dilute solution, where the osmotic pressure opposing the solution pressure is smaller, and is deposited from the concentrated solution. The current is transported through the liquids by both ions, $Ag^{\cdot}$ and NO_3', and the scheme in Fig. 41 and the table below shows that the nett result of the passage of $1F$ is the transport of n mols of $AgNO_3$ from the strong to the weak solution, where n is the transport number of the anion (NO_3').

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[1] On the subject of heats of ionisation, see Ostwald, "Lehrbuch," II., i., 949 ff. Herzfeld, *A. P.*, 1918, **56**, 133. On the thermodynamics of the Volta, Thermoelectric and Thermionic effects, see Bridgman, *P. R.*, 1919, **14**, 306.

[2] "Scientific Papers," 1889, p. 180.

VESSEL A.—*Weak Solution.*

Gains 1 equiv. Ag by dissolution from the electrode.

Loses $1 - n$ equiv. Ag by migration.

Gains n equiv. NO_3 by migration.

Nett gain = n equiv. $AgNO_3$.

VESSEL B.—*Strong Solution.*

Gains $1 - n$ equiv. Ag by migration.

Loses 1 equiv. Ag by deposition.

Loses n equiv. NO_3 by migration.

Nett loss = n equiv. $AgNO_3$.

The osmotic work of transferring n mols of salt from the concentration c_1 (strong solution) to the concentration c_2 (weak solution) is $2n\text{RT} \ln (c_1/c_2)$, since *two* ions are formed from 1 mol of salt. Thus $\text{E}F = 2n\text{RT} \ln (c_1/c_2)$, or :

$$\text{E} = \frac{2n\text{RT}}{F} \ln \frac{c_1}{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [307]$$

If the ion concentrations are in the ratio of 1 : 10, then, since $n = 0{\cdot}528$ for $AgNO_3$, $\text{E} = 2 \times 0{\cdot}528 \times 0{\cdot}058 \times \log 10 = 0{\cdot}061$ volt at 18°. This equation also applies in non-aqueous solvents.[1]

113. General Equation for the E.M.F. of a Reversible Cell.—The *affinity* of a reaction :

$$n_1\text{A}_1 + n_2\text{A}_2 + \dots = n_1'\text{A}_1' + n_2'\text{A}_2' + \dots$$

is given by equation [240] :

$$\text{A}_\text{T}' = \text{RT} \ln \text{K} - \text{RT}\Sigma n_1 \ln \text{C}_1$$

where C_1 is a free concentration, as explained in § 83, and K is the equilibrium constant :

$$c_1'^{n_1'} \, c_2'^{n_2'} \dots / c_1^{n_1} \, c_2^{n_2} \dots$$

But if a cell is reversible, and the reaction takes place in it so as to yield current, then :

$$\text{A}_\text{T}' = y\text{E}F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (308)$$

where y denotes the number of F's transported through the cell when the reaction occurs. Thus, since the value of A_T' is independent of the process :

$$\left.\begin{aligned} \text{E} = \text{A}_\text{T}'/yF &= \frac{\text{RT} \ln \text{K} - \text{RT}\Sigma n_1 \ln \text{C}_1}{yF} \\ &= \frac{0{\cdot}0002\text{T}}{y} \log \frac{\text{KC}_1^{n_1} \, \text{C}_2^{n_2} \dots}{\text{C}_1'^{n_1'} \, \text{C}_2'^{n_2'} \dots} \text{ volts} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad [309]$$

which is the most general formula for the E.M.F. of a reversible cell, on the assumption of the gas laws. By making use of equation (304) this last restriction may be removed.

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[1] Cf. Lapworth and Partington, *C. S.*, 1911, 99, 1417 ; Partington and Grant, *F. S.*, 1923, 19, 414.

As an example of the application of the formula consider the calculation of the potential of an *oxidation* or *reduction* electrode. The equations:

$$\mathrm{Fe}^{\cdot\cdot} + \oplus \longrightarrow \mathrm{Fe}^{\cdot\cdot\cdot} \qquad 2\mathrm{Cl}' + 2\oplus \longrightarrow \mathrm{Cl}_2$$

$$\mathrm{Cu}^{\cdot} + \oplus \longrightarrow \mathrm{Cu}^{\cdot\cdot} \qquad \mathrm{FeCy}_6'''' + \oplus \longrightarrow \mathrm{FeCy}_6'''$$

show that, in reactions involving ions, *oxidation* is equivalent to increase in positive charge, or decrease in negative charge, and *reduction* is equivalent to decrease in positive charge, or increase in negative charge.

Consider the oxidising power of the chromic acid electrode. The reaction is:

$$\mathrm{CrO}_4'' + 8\,\mathrm{H}^{\cdot} = \mathrm{Cr}^{\cdot\cdot\cdot} + 4\mathrm{H}_2\mathrm{O} + 3\oplus.$$

Here $y = 8 - 2 - 3 = +3$, and $[\mathrm{H_2O}]$ is constant[1]

$$\therefore \quad \mathrm{E} = \frac{0{\cdot}0002\mathrm{T}}{3} \log \frac{\mathrm{K}[\mathrm{CrO}_4''] \times [\mathrm{H}^{\cdot}]^8}{[\mathrm{Cr}^{\cdot\cdot\cdot}] \times [\mathrm{H_2O}]^4}$$

$$= \frac{0{\cdot}0002\mathrm{T}}{3} \log \frac{\mathrm{K}'[\mathrm{CrO}_4''] \times [\mathrm{H}^{\cdot}]^8}{[\mathrm{Cr}^{\cdot\cdot\cdot}]}.$$

In reality this electrode is not reversible.

The reducing power of hydroquinone is represented by[2]:

$$\mathrm{C_6H_4(OH)_2} = \mathrm{C_6H_4O_2}\ (\text{quinone}) + 2\mathrm{H}^{\cdot} - 2\oplus$$

$$\mathrm{E} = -\frac{0{\cdot}0002\mathrm{T}}{2} \log \frac{\mathrm{K}[\mathrm{C_6H_4(OH)_2}]}{[\mathrm{C_6H_4O_2}] \times [\mathrm{H}^{\cdot}]^2}.$$

Changes of free energy determined by electrode potential measurements are, of course, additive in the same sense as intrinsic energy changes according to Hess's law.

Luther's Rule.—An important relation between the electro-affinities of a material with several stages of oxidation was deduced by Luther.[3] Let the lowest, intermediate, and highest stages of oxidation be denoted by l, m, h, then:

$$\Delta\mathrm{F}(l \rightarrow h) = \Delta\mathrm{F}(l \rightarrow m) + \Delta\mathrm{F}(m \rightarrow h),$$

the free energy change for 1 mol from the lowest to the highest stage of oxidation being independent of the path, and therefore equal to the sum of the two changes *viâ* the intermediate stage. If a, b, are the valencies of the two ions, and $\mathrm{E}^\circ(l \rightarrow h)$, $\mathrm{E}^\circ(l \rightarrow m)$, $\mathrm{E}^\circ(m \rightarrow h)$ are the electro-affinities: $\Delta\mathrm{F}(l \rightarrow m) = aF\mathrm{E}^\circ(l \rightarrow m)$, and two corresponding equations

$$\therefore \quad \mathrm{E}^\circ(l \rightarrow h) = [a\mathrm{E}^\circ(l \rightarrow m) + (b - a)\,\mathrm{E}^\circ(m \rightarrow h)]/b \quad . \quad (310)$$

When the three forms are in equilibrium:

$$\mathrm{E}(l \rightarrow h) = \mathrm{E}(l \rightarrow m) = \mathrm{E}(m \rightarrow h) \quad . \quad . \quad . \quad (311)$$

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[1] Concentrations are expressed by the symbols in square brackets.

[2] Granger and Nelson, *J. A. C. S.*, 1921, **43**, 1401; Conant and Fieser, *ibid.*, 1922, **44**, 1382, 2480; La Mer and Baker, *ibid.*, 1922, **44**, 1954.

[3] Luther and Wilson, *Z. p. C.*, 1900, **34**, 488; Luther, *ibid.*, 1901, **36**, 385.

114. **The Oxy-hydrogen Cell.**—An important cell is that formed of the hydrogen and oxygen electrodes. The maximum work of the reaction:

$$2H_2 + O_2 = 2H_2O(\text{liq.})$$

is (omitting external work, which is not electro-motively active):

$$A_T' = RT \ln K' - RT\Sigma n_1 \ln p_1 \text{ from (245a),}$$

hence:

$$E = \frac{RT}{4F} \ln (K' \, p^2_{H_2} \, p_{O_2}/p^2_{H_2O})$$

where $K' = (p^2_{H_2O})/\pi^2_{H_2} \, \pi_{O_2}$; p_{H_2} and p_{O_2} are the pressures of the free gases; π_{H_2} and π_{O_2} are the (extremely small) partial pressures of hydrogen and oxygen in equilibrium with water vapour at the temperature of the cell. If we assume that the pressures of the free H_2 and O_2 are equal to 1 atm., we find:

$$E = \frac{0{\cdot}0002T}{4} \log \frac{1}{\pi^2_{H_2} \, \pi_{O_2}} \quad . \quad . \quad . \quad . \quad [312]$$

an equation deduced by Nernst and Wartenberg in 1906.[1]

The values of π_{H_2} and π_{O_2} can be calculated from a formula derived from direct measurements of the dissociation of steam at high temperatures (see § 88) by extrapolation. At 17° C. = 290° abs. we find from this formula that $0{\cdot}466 \times 10^{-25}$ per cent. of the steam is dissociated at 1 atm. pressure. The vapour pressure of water at 17° C. is 0·0191 atm., and since $K' = \frac{p}{RT} \cdot \frac{x^3}{2}$ when x, the extent of dissociation, is small, it follows that x is inversely proportional to $\sqrt[3]{p}$. Thus, under its own vapour pressure, water vapour is dissociated at 17° C. to the extent of $0{\cdot}466 \times 10^{-25}/\sqrt[3]{0{\cdot}0191} = 1{\cdot}75 \times 10^{-25}$ per cent. Thus $\pi_{H_2} = 0{\cdot}0191 \times 1{\cdot}75 \times 10^{-25}$ atm., and $\pi_{O_2} = 0{\cdot}5 \times 0{\cdot}0191 \times 1{\cdot}75 \times 10^{-25}$ atm. The substitution of these values in [312] gives $E = 1{\cdot}233$ volt.

This value is at least 0·1 volt higher than the measured value of the E.M.F. of the cell. The discrepancy has been traced to the fact that the oxygen electrode is not reversible, and the true E.M.F. of the cell has been determined indirectly in the following way.

G. N. Lewis[2] measured the E.M.F. of the cell: Ag/Ag_2O in alkali soln./H_2, and from the extrapolated dissociation pressure curve of Ag_2O calculated the partial pressure of O_2 over Ag_2O

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[1] *Z. p. C.*, 1906, **56**, 534.

[2] *Z. p. C.*, 1906, **55**, 449.

at the temperature of the experiment. From the E.M.F. he was then able to calculate the value of the E.M.F. when the partial pressure of the oxygen was 1 atm., and found 1·217 at 25° C. The corresponding value from Nernst and Wartenberg's results would be at 25° C. 1·225 volts, since these observers calculated the change of E.M.F. with temperature according to the formula $E = 1{\cdot}232 - 0{\cdot}00085\ (t^\circ \text{ C.} - 17)$. Brönsted [1] used the cell: Hg/HgO in alkali soln./H_2, and by using the dissociation pressure results of Pélabon at higher temperatures and extrapolating, found 1·227 volt at 25° C.

The slight discrepancy between Lewis's values and the others was cleared up by Rördam (1921),[2] who found that there are two forms of silver oxide, and the dissociation pressure measurements of Lewis were made on one form, stable at higher temperatures, whilst the E.M.F. measurements were made with the other form, stable at lower temperatures. The correction brings Lewis's results into absolute agreement with those of Brönsted and of Nernst and Wartenberg.[3]

The Lead Accumulator.—The reaction taking place in the lead accumulator is: $PbO_2 + Pb + 2H_2SO_4 \rightleftharpoons 2PbSO_4 + 2H_2O$. When *two* cells, with different concentrations of acid, are coupled together, the result is equivalent to the passage of 2 mols of H_2SO_4 from the first to the second, and $2H_2O$ from the second to the first, for each $2F$ transported. Let p_1, p_2 be the partial pressures of the acid, P_1, P_2 those of the water, in the two acids, then the work done per F transported is given by [275]:

$$\Delta E\,.\,F = RT\left(\ln\frac{p_1}{p_2} + \ln\frac{P_2}{P_1}\right)$$

where ΔE is the difference in voltage of the two cells. The values of P_1, P_2 are known, but p_1 and p_2 are too small to be measured directly. We therefore integrate (277) by parts:

$$\ln\frac{p_0}{p} + x\ln\frac{P_0}{P} = \int_0^x \ln\frac{P_0}{P}\,dx$$

∴ for the two solutions:

$$\ln\frac{p_1}{p_2} = x_2\ln P_2 - x_1\ln P_1 - \int_{x_1}^{x_2} \ln P\,dx$$

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[1] *Z. p. C.*, 1909, **65**, 84, 744.

[2] Cf. *Z. p. C.*, 1921, **99**, 474.

[3] Keyes and Hara, *J. A. C. S.*, 1922, **44**, 479.

$$\therefore \quad \Delta E = \frac{RT}{F}\left(x_2 \ln P_2 - x_1 \ln P_1 - \int_{x_1}^{x_2} \ln P\,dx + \ln \frac{P_2}{P_1}\right) \quad . \ [313]$$

which was found by Dolezalek (1898) [1] to give values of ΔE in good agreement with the measured values.

EXAMPLES XVI.

1. The E.M.F. of the cell Ag, AgCl/KCl(*n*.)/HgCl, Hg is 0·04551 volt at 24·86° C. and 0·04215 volt at 14·86° C. Calculate the heat of reaction of the cell (in cals./equivalent) at 19·86° C. Calculate also the latent heat of the cell in joules.

2. The temperature coefficient of the cell $Pb/Pb^{++}/Pb(Hg), Pb$, is 0·000016 volt per 1° C. (Gerke), and its E.M.F. at 25° C. = 0·0057 volt. Calculate (i.) the latent heat of the cell at 25° C.; (ii.) the heat of reaction at this temperature; (iii.) the change in entropy; and (iv.) the free energy change.

3. The diminution of thermodynamic potential in the formation of liquid water from its elements is 37,455 cals. at 25° C. Assuming the electrode potential of the H_2 electrode to be zero at this temperature, and that the thermodynamic potential change when 1 mol H_2O is formed from its ions is 19,105 cals. at 25° C., show that the electrode potential, $Pt/OH'/O_2$, is + 0·397 volt.

4. Ogg (1898) found the E.M.F. of the cell Hg/Hg_2Cl_2, *n*.KCl/0·1*n*. $\frac{1}{2}Hg_2(NO_3)_2$ + *n*.HNO_3/Hg to be 0·466 volt. What is the concentration of $Hg^{\cdot\cdot}$ ions in saturated Hg_2Cl_2 solution?

5. The latent heat of transition of white tin into grey tin is 9,550 gm. cals. Calculate dE/dT for the cell: white Sn/$SnCl_4$sol./grey Sn at 18° C.; the transition point. (*N.B.* At the transition temperature the two modifications of Sn are in equilibrium, hence the electrical work done in the cell is zero.

6. Find the E.M.F. of the cell Tl/TlI sat. soln./TlCl sat. soln./Tl at 25° C., if the concentrations of the Tl ions in the chloride and iodide solutions are 0·01409 *n*. and 0·000235 *n*. respectively.

Calculate also the E.M.F. of the cell Pt/I_2 sat. soln. in 0·1 *n*.KI/TlI sat. + I_2/Pt at 25° C., given that the concentration of the iodide ion in 0·1 *n*.KI soln. saturated with I_2 is 0·04267 *n*.

7. Assuming the data in question 6, and given that the E.M.F. of the cell Tl/sat. TlCl soln./0·1 *n*.KCl + Hg_2Cl_2/Hg is 0·7816 volt and that of the cell Hg/Hg_2Cl_2 + 0·1 *n*.KCl/0·1 *n*.KI + sat. I_2/Pt is 0·2835 volt (both at 25° C.), find the free energy of the reaction Tl (solid) + $\frac{1}{2}I_2$ (solid) = TlI solid.

8. The Clark cell at 18° C. has an E.M.F. of 1·4291 volts; this falls off with the temperature at the rate of 0·0012345 volts per 1° C. Calculate the latent heat of the cell together with the thermodynamic potential change; thence find the heat of the reaction $Zn + Hg_2SO_4 = 2Hg + ZnSO_4$.[2]

9. The E.M.F. of the cell Cu/$Cu(NO_3)_2$ soln. hot/$Cu(NO_3)_2$ soln. cold/Cu shows that dE/dT for this cell is 0·00072 at 291° K. Show that the positive pole of the Daniell cell cools during action.

10. Calculate the heat of ionisation of zinc given that dE/dT at 18° C. of the cell Zn/hot $Zn^{\cdot\cdot}$ soln./cold $Zn^{\cdot\cdot}$ sol./Zn is 0·0007.

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[1] *A. P.*, 1898, **65**, 894; *Z. p. C.*, 1898, **26**, 321; Whetham, "Theory of Solution," 1902, p. 265; cf. R. Thibaut, *Z. E.*, 1913, **19**, 881; Féry, *J. P.*, 1916, **6**, 21, 187.

[2] For the discrepancy between this value and the value calculated by thermal methods, 233,000 joules, see Lehfeldt, "Electro-chemistry," London, 1908, p. 187.

11. Calculate the heat of ionisation of Cu at 27° C., given dE/dT = 0·00072 volt/° C. for the Cu electrode.

12. The E.M.F. of the cell Ag (metal)/sat. AgCl soln./Cl_2 (gas) is 1·132 volts at 17° C., the Cl_2 being under atmospheric pressure. The heat of the reaction Ag (metal) + Cl (gas) = AgCl (amorph.) is 29,380 cals. (Thomsen). Calculate the change of thermodynamic potential for the cell; also the entropy change at 17° C. Find also the dissociation pressure of AgCl in atmospheres at 17° C.

13. Calculate the E.M.F. of the cell in which the reaction $SCN' + TlCl \rightleftharpoons Cl' + TlSCN$ occurs at 20° C., with concentrations of SCN′ and Cl′ in the ratios 0·84 and 1·52, given $K = [Cl']/[SCN'] = 1{\cdot}24$.

Find also the affinities in the two cases.

14. The E.M.F. of the cell Ag/sat. AgCl soln./Cl_2 is 1·132 volts at 17° C. If the decomposition potentials of Ag and Cl_2 are + 0·784 volt and + 1·3600 volts respectively (H_2 electrode as unit), find the solubility of AgCl at 17° C.

Calculate also the dissociation pressure of AgCl at this temperature.

15. In the case of cells consisting of Na amalgam electrodes of two different concentrations transfer of sodium takes place from the more concentrated to the more dilute amalgam. Calculate the total energy change per mol involved in the latter process from the following figures (Richards and Conant) obtained at 25° C.:

	Sodium:			
	C_1%.	C_2%.	dE/dT.	E (in volts).
(*a*)	0·416	0·1978	0·0000915	0·03577
(*b*)	0·416	0·1102	0·000155	0·05738
(*c*)	0·1978	0·0396	0·0001625	0·05312
(*d*)	0·0396	0·01972	0·000061	0·01943

16. Pearce and Hart found the E.M.F. of the cell Ag/AgBr, KBr soln./K(Hg) to be as follows (c = conc. of KBr in mols per litre):

	c.	E (25°).	E (30°).	E (35°).
(*a*)	2·5000	2·8032	2·0235	1·9948
(*b*)	1·0000	2·0792	2·0657	2·0518
(*c*)	0·5000	2·1108	2·0976	2·0849
(*d*)	0·2500	2·1432	2·1308	2·1179
(*e*)	0·1000	2·1858	2·1740	2·1624

Calculate for each temperature and concentration the thermodynamic potential decrease in joules.

If the decrease of Z at any temperature t, $(-\Delta Z)_t$, is connected with that at any other temperature θ by the relation

$$(-\Delta Z)_t = (-\Delta Z)_\theta[1 + \alpha(t - \theta) + \beta(t - \theta)^2]$$

find the value of the constants α and β for each concentration. Thence deduce the enthalpy decrease accompanying the cell-reaction at 25° C. ($F = 96{,}494$).

17. The following table represents the E.M.F.'s of cells consisting of two electrodes of concentrated and dilute Na amalgam measured by Richards and Conant (1922):

	E.M.F. in Millivolts.		
	15°.	25°.	35°.
Cell A	34·84	35·77	36·67
Cell B	55·82	57·38	58·92
Cell C	51·48	53·12	54·73
Cell D	18·84	19·43	20·05

Calculate the average value of dE/dT for each cell.

18. According to the double sulphation theory the reaction taking place in the lead accumulator is $Pb + 2H_2SO_4 + PbO_2 = 2PbSO_4 + 2H_2O$. The heats of formation of $PbSO_4$, H_2O, H_2SO_4 and PbO_2 are 112,970; 68,360; 89,680; and 31,150 gm. cals. respectively. The heat of infinite dilution of sulphuric acid is 17,835 gm. cals. Calculate the E.M.F. of an accumulator (a) when conc. H_2SO_4 is used, and (b) when very dilute H_2SO_4 is used.

19. According to Luther's rule:

$$E_{\text{Cu metal} \rightarrow Cu^{\cdot\cdot}} = \frac{E_{Cu + Cl' \rightarrow CuCl} + E_{CuCl \rightarrow Cu^{\cdot\cdot} + Cl'}}{2}$$

$$= \frac{E_{Cu + Br' \rightarrow CuBr} + E_{CuBr \rightarrow Cu^{\cdot\cdot} + Br'}}{2}.$$

The electro-affinity of $Cu/CuCl + KCl$ is $+ 0{\cdot}4870$ volt; similarly, the electro-affinity of the electrode $Cu/CuBr + KBr$ is $+ 0{\cdot}4055$ volt. The potential of the electrode $Pt/CuCl + CuSO_4 + KCl$, the Cl' concentration being 0·925, is $+ 0{\cdot}6375$ volt and that of the electrode $Pt/CuBr + CuSO_4 + KBr$, the Br' concentration being 0·93, $+ 0{\cdot}7205$ volt. Taking $T = 18°$ C., find whether the rule holds for these electrodes.

20. Brönsted measured the E.M.F.'s at different temperatures of the cell Pb/satd. $PbCl_2$ soln. $+ AgCl/Ag$. Halla found that the results could be expressed by the formula:

$$E = 11{,}904 - 1{\cdot}0062 \times 10^{-2}T^2 + 8{\cdot}55066 \times 10^{-6}T^3$$

E being the electrical work in calories. Find the heat of the reaction at constant pressure, $Pb + 2AgCl = PbCl_2 + 2Ag$ at 27° C.

CHAPTER XVII

Nernst's Theorem

115. **Nernst's Theorem.**—It has been explained (§ 82) that Berthelot's Principle of Maximum Work, which amounts to the assumption that the heat evolved in a chemical change (Q) is a measure of the affinity, is not in general strictly true. A correct measure of the affinity is supposed to be given by the diminution of free energy, $F_1 - F_2 = A$, rather than the diminution of intrinsic energy, $U_1 - U_2 = Q$, and the principle of maximum work (§ 82) in the form :

$$A_T = Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (218)$$

must then be replaced by the maximum work equation :

$$A_T = Q + T \, . \, dA_T/dT \quad . \quad . \quad . \quad . \quad . \quad (197)$$

The term $T \, . \, dA_T/dT$ may be regarded as a correction to the principle of Berthelot. In some cases it may be negligibly small, in others very appreciable (see § 76).

A particularly striking case of the different results obtained by these two equations is furnished by a chemical reaction between gases, where the value of A_T is very largely dependent on the concentrations, as is seen from equation [238], whilst the heat of reaction is practically independent of these. In cases where there are very variable concentrations, therefore, the principle of Berthelot fails.

In other cases the principle of Berthelot gives results very approximately correct [1] (§ 82). The correct interpretation of the equation and the formulation from it of a new principle in thermodynamics we owe to Nernst. The latter, in 1906, remarked that, since dA_T/dT remains finite, A_T and Q are necessarily equal at the absolute zero ($T = 0$ in 197), and in many cases they are *approximately* equal even at other temperatures, not too high.[1] The curves representing $\mathrm{A_T}$ and Q as functions of temperature then approach asymptotically in the neighbourhood of the absolute zero, as shown in Fig. 42.[2]

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[1] Berthelot himself limited the application of his principle to *solids*, in which case it is approximately correct ("Thermochimie," I., p. 10), and also pointed out that it would be more exact at very low temperatures (*ibid.*, p. 12). He also defines "chemical heat," to which the principle applies, as that transformable into work, *i.e.*, really *free energy*.

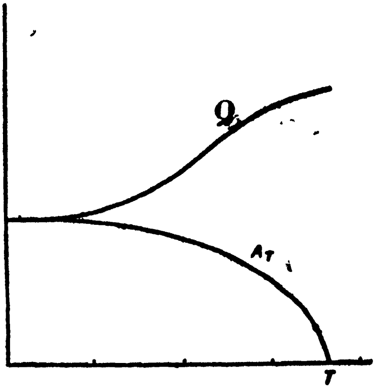

FIG. 42.

In this case the relation :

$\lim d\mathrm{A_T}/d\mathrm{T} = \lim dQ/d\mathrm{T}$ for $\mathrm{T} = 0$

is assumed, and this may be called the *Theorem of Nernst.*

In the first place this will hold good only for reactions between *pure liquid or solid materials,* not, as we have seen, for reactions between gases, and cases of variable concentration, although the principle may be extended to reactions between gases. Its application to solutions awaits development.

We may also consider the part played by Nernst's theorem in thermodynamics from another point of view. In such cases as the relation between the equilibrium constant and temperature :

$$d \ln \mathrm{K}/d\mathrm{T} = \mathrm{Q}_v/\mathrm{RT}^2 \quad . \; . \; . \; . \; . \quad [247]$$

the integration :

$$\ln \mathrm{K} = -\mathrm{Q}_v/\mathrm{RT} + \mathit{const.} \quad . \; . \; . \; . \quad [251]$$

introduces an unknown constant. Nernst's theorem, as we shall see, enables us to calculate this constant, and thus supplements the two laws of thermodynamics.

116. Formulation of Nernst's Theorem.—The two forms of the maximum work equation given in (197) and (206) may be represented without suffixes ($Q = -\mathrm{Q}$) :

$$\mathrm{A} + \mathrm{Q} = \mathrm{T} \,.\, d\mathrm{A}/d\mathrm{T} \text{ or } \mathrm{A} - Q = \mathrm{T} \,.\, d\mathrm{A}/d\mathrm{T} \quad . \; . \; . \; . \; . \quad (314)$$

But
$$\frac{d}{d\mathrm{T}}\left(\frac{\mathrm{A}}{\mathrm{T}}\right) = \frac{1}{\mathrm{T}} \cdot \frac{d\mathrm{A}}{d\mathrm{T}} - \frac{\mathrm{A}}{\mathrm{T}^2} = \frac{\mathrm{Q}}{\mathrm{T}^2} \quad . \; . \; . \; . \quad (315)$$

$$\therefore \quad \mathrm{A} = \mathrm{T}\int \frac{\mathrm{Q}}{\mathrm{T}^2}\, d\mathrm{T} \quad . \; . \; . \; . \; . \; . \quad (316)^{3}$$

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[1] The criticism of Berthelot's principle by Ostwald ("Watts' Dictionary of Chemistry," ed. Morley and Muir, vol. i., 1890, p. 86) is far too sweeping.

[2] On a method of tracing the A and Q curves, see Nernst, "Grundlagen des neuen Wärmesatzes," p. 70.

[3] Integration of (316) mechanically : Gans and Miguez, *P. Z.*, 1915, **16**, 247.

If A_0, Q_0 are the values for $\mathrm{T} = 0$, and if $d\mathrm{A}/d\mathrm{T}$ is never infinite, (314) shows that:

$$\mathrm{A}_0 = -\mathrm{Q}_0 = \mathcal{Q}_0 . \quad . \quad . \quad . \quad . \quad . \quad (317)$$

Berthelot's rule is therefore always true at the absolute zero.[1]

To find the limiting value of:

$$d\mathrm{A}/d\mathrm{T} = (\mathrm{A} - \mathcal{Q})/\mathrm{T}$$

at the absolute zero, differentiate the numerator and denominator of the fraction on the right with respect to T, and then put $\mathrm{T} = 0$.[2] Thus:

$$\operatorname*{Lim}_{\mathrm{T}=0} \frac{d\mathrm{A}}{d\mathrm{T}} = \operatorname*{Lim}_{\mathrm{T}=0} \frac{d\mathrm{A}}{d\mathrm{T}} - \operatorname*{Lim}_{\mathrm{T}=0} \frac{d\mathcal{Q}}{d\mathrm{T}}$$

$$\therefore \quad \operatorname*{Lim}_{\mathrm{T}=0} \frac{d\mathcal{Q}}{d\mathrm{T}} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (318)$$

Thus from (38): $\quad \Gamma_i - \Gamma_f = 0, \text{ when } \mathrm{T} = 0 \quad . \quad . \quad . \quad . \quad . \quad (319)$

This result agrees with the quantum theory, according to which all the *separate* values of the specific heats in Γ_i and Γ_f are equal to zero when $\mathrm{T} = 0$ (§ 130).

Nernst then assumes that:

$$\textbf{Lim } d\mathrm{A}/d\mathrm{T} = \textbf{Lim } d\mathcal{Q}/d\mathrm{T}, \textbf{ when } \mathrm{T} = 0 \quad . \quad (320)$$

Equations (318) and (320) show that:

$$\textbf{Lim } d\mathrm{A}/d\mathrm{T} = 0, \textbf{ when } \mathrm{T} = 0 \quad . \quad . \quad . \quad (321)$$

which may be taken as the expression of *Nernst's Theorem.*

117. Maximum Work and Heat of Reaction.—Assume that the heat of reaction may, as usual, be represented as a function of temperature of the form:

$$\mathcal{Q} = \mathcal{Q}_0 + a\mathrm{T} + \beta\mathrm{T}^2 + \gamma\mathrm{T}^3 + \ldots \quad . \quad . \quad (322)$$

where $a, \beta, \ldots$ are constants (cf. § 22).[3]

Then $\quad d\mathcal{Q}/d\mathrm{T} = \Gamma_i - \Gamma_f = a + 2\beta\mathrm{T}$

$\therefore$ from (318) $a = 0$ and

$$\mathcal{Q} = \mathcal{Q}_0 + \beta\mathrm{T}^2 + \ldots \quad . \quad . \quad . \quad . \quad (323)$$

It is usually sufficient to omit terms after T^2 in (322):

$$d(\mathrm{A}/\mathrm{T})/d\mathrm{T} = -\mathcal{Q}/\mathrm{T}^2 = -(\mathcal{Q}_0 + \beta\mathrm{T}^2)/\mathrm{T}^2$$

$\therefore$ by integration $\mathrm{A} = \mathcal{Q}_0 - \beta\mathrm{T}^2 + \textit{const.} \times \mathrm{T}$.

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[1] $\mathrm{Q}_{op} = \mathrm{Q}_{ov}$, since at $\mathrm{T} = 0$ the external work vanishes.

[2] See Edwards' "Differential Calculus" (London, 1912), p. 376.

[3] Cf. F. Jüttner, *Z. E.*, 1911, **17**, 139.

Differentiate with respect to T and put T = 0. Then, from (321), it follows that *const.* = 0

$$\therefore\ A = Q_0 - \beta T^2 \quad \ldots\ldots\ldots \quad (324)$$

Equations (323) and (324) are not in accord with the quantum theory of specific heats, but are useful approximations.[1] At *very* low temperatures, with reactions between pure solids, Debye's theory (§ 136) gives, *exactly:*

$$\left.\begin{aligned} Q &= Q_0 + \beta' T^4 \\ A &= Q_0 - \tfrac{1}{3}\beta' T^4 \end{aligned}\right\} \quad \ldots\ldots \quad (325)$$

As an application of the above equations consider the calculation of the *transition temperature*, T_0, of:

rhombic sulphur $\rightleftarrows$ monoclinic sulphur.

At this temperature there is equilibrium between the two phases, and the vapour pressures are equal,

$$\therefore\ A = Q_0 - \beta T_0^2 = 0.$$

But $Q = Q_0 + \beta T^2 = 50{\cdot}4 + 3{\cdot}69 \times 10^{-4}\, T^2$, as found from the experimental values of the specific heats and the heat of transition, hence:

$$A = 50{\cdot}4 - 3{\cdot}69 \,.\, 10^{-4} T_0^2 = 0$$

$\therefore\ T_0 = (\sqrt{50{\cdot}4/3{\cdot}69 \times 10^{-4}}) = 369{\cdot}5°$ K. (obs. 368·4°; the very close agreement is accidental).[2]

As a further application we may calculate the E.M.F. of the Clark cell[3] at the cryohydric point, when ice separates and all the substances taking part in the reaction:

$$Zn + Hg_2SO_4 + 7H_2O(\text{ice}) = ZnSO_4{,}7H_2O + 2Hg + 2Q$$

are pure substances.

Calculation of Q: heats of formation:

(Zn, S, 4O) = 230,090 cal.
(2Hg, S, 4O) = 175,000 cal.
($ZnSO_4{,}7H_2O$ liq.) = 22,690 cal.
H_2O(liq.) = H_2O (solid) at 17° C. (extrapolated) + 1580 cal.

$\therefore\ 2Q = 230{,}090 + 22{,}690 - (175{,}000 + 7 \times 1580) = 66{,}720$ cal. at 17° C.

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[1] Cf. Nernst, *B. B.*, 1909, p. 247.

[2] Tin, cf. Brönsted, *Z. p. C.*, 1914, **88**, 479.

[3] Cf. Pollitzer, *Z. E.*, 1911, **17**, 5; "Berechnung Chem. Affinitäten nach dem Nernstschen Wärmetheorem," 1912, p. 149; Nernst, "Grundlagen des neuen Wärmesatzes," 1919, pp. 87, 95; Halla, *Z. E.*, 1908, **14**, 411; Fischer, *Z. an. C.*, 1912, **78**, 41; Braune and Koref, *ibid.*, 1914, **87**, 175.

Calculation of β: specific heats:

Molecular heats: Zn = 6·0 (10°); Hg_2SO_4 = 31·0 (50°); $7H_2O$ (ice) = 63·7 (10° extrapol.); $ZnSO_4,7H_2O$ = 89·4 (10°); 2Hg = 13·2 (10°).

$$2Q = 2Q_0 + 2\beta T^2 \therefore 2\,dQ/dT = 4\beta T = \Gamma_i - \Gamma_f$$

$= (6 + 31{\cdot}0 + 63{\cdot}7) - (89{\cdot}4 + 13{\cdot}2) = -1{\cdot}9$ for $T = 283°$,
$\therefore 4\beta = -1{\cdot}9/283$, or $\beta = -0{\cdot}0017$.

Calculation of Q_0:

Thus $\quad Q = Q_0 + \beta T^2 = 66{,}720/2$ at $T = 290$

$$\therefore \quad Q_0 = 33{,}360 + (290)^2 \times 0{\cdot}0017 = 33{,}505 \text{ cal.}$$

Calculation of A:

$$A = Q_0 - \beta T^2 = 33{,}505 - 0{\cdot}0017\ T^2 \text{ cal.}$$

At the cryohydric point, T = 266° K.

$$A_{266} = 33{,}505 + 0{\cdot}0017 \times (266)^2 = 33{,}625 \text{ cal.}$$

Thus E = 33,625/23,064 = 1·459 volt, which is very near the observed value.[1]

118. Application to Gaseous Reactions.—Nernst's theorem does not directly apply to reactions in which gases take part, but it is easy to apply it by indirect methods to this case, and if the new theory of gases is true (§ 140) it may apply directly.

The principle of the method may be illustrated by an example. The affinity of the reaction $2Ag + I_2 = 2AgI$ may be calculated from the equation $A = Q_0 - \beta T^2$. It may also be calculated from the equation $A = RT \ln (p_0/p)$, where p_0 is the vapour pressure of solid iodine at the given temperature, and p is the dissociation pressure of silver iodide. Thus, if we know the vapour pressure curve of solid iodine at various temperatures, a combination of the two equations (the first involving Nernst's theorem) will enable us to find the dissociation pressures of silver iodide at various temperatures.

119. Vapour-pressure Curve at Low Temperatures.—It is obvious from the discussion in the previous paragraph that it is important to know the vapour pressure curves of pure substances at low temperatures (when $A = Q_0 - \beta T^2$ applies approximately). At low temperatures, p is small, and the ideal gas law $pv = RT$, or $p = cRT$, may always be applied. But, from [82]:

$$\lambda \text{ (absorbed)} = RT^2 . d \ln p/dT$$

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[1] Cf. Seibert, Hulett and Taylor, *J. A. C. S.*, 1917, **39**, 38.

Assume $\lambda = \lambda_0 + a_0 T + \beta_0 T^2 + \ldots$ for a pure substance

$$\therefore \quad \ln p = -\lambda_0/RT + a_0 \ln T/R + \beta_0 T/R + \gamma_0 T^2/2R + \ldots + i \quad \ldots\ldots \quad [326]$$

where i is the constant of integration. Hence, if $i' = i - \ln R$:

$$\ln c = -\lambda_0/RT + (a_0/R - 1)\ln T + \beta_0 T/R + \gamma_0 T^2/2R + i' \quad [327]$$

To find the value of i we must know λ as a function of T at very low temperatures (since then we know λ_0, a_0, β_0, etc.), and *one* value of p or c. At very low temperatures, however, we can neglect the terms involving powers of T in [326], and since i is independent of T:

$$\therefore \qquad \ln p = -\lambda_0/RT + a_0 \ln T/R + i \quad \ldots \quad [328]$$

$$\text{Now } \lambda = Q_v + RT \quad \therefore \quad d\lambda/dT = dQ_v/dT + R$$
$$= C_v \text{ (vapour)} - C \text{ (solid)} + R$$
$$= C_p \text{ (vapour)} - C \text{ (solid)}$$

where C denotes the molecular heat of the condensed phase.

But $\lambda = \lambda_0 + a_0 T \quad \therefore \quad a_0 = d\lambda/dT = C_p$ (vapour) $-$ C (solid). At very low temperatures, $C = 0$, as we shall see, and for *all* gases the quantum theory (§ 137) gives $C_p = 5/2 \,.\, R$ at very low temperatures, since all gases then behave like monatomic gases, for which $C_v = 3/2 \,.\, R$ and $\therefore\ C_p = 5/2 \,.\, R$. Thus:

$$\boldsymbol{\ln p = -\lambda_0/RT + 5/2 \,.\, \ln T + i} \quad \ldots \quad \mathbf{[329]}$$

may be taken as the form of the vapour pressure curve of all pure substances *at very low temperatures.*

More generally, the equations:

$$d \ln p/dT = \lambda/RT^2 \text{ and } \lambda = \lambda_0 + \int (C_p - C)\, dT \text{ give}^{1}:$$

$$\ln p = -\frac{\lambda_0}{RT} + \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T (C_p - C)\, dT + i \quad . \quad [330]$$

[illegible] to Langen,[2] the value C_p may be split into a translational term independent of T and equal to 2·5R for a diatomic gas and a rotational term C_{pr}, dependent on T:

$$\ln p = -\frac{\lambda_0}{RT} + \frac{5}{2}\ln T + \frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T (C_{pr} - C)\, dT + i \,. \quad [330a]$$

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[1] Partington, "Thermodynamics," 1913, p. 493.

[2] *Z. E.*, 1919, **25**, 25.

The assumption that C_{pr} is very small at low temperatures gives:

$$\ln p = -\frac{\lambda_0}{\mathrm{RT}} + \frac{5}{2}\ln \mathrm{T} - \frac{1}{\mathrm{R}}\int_0^{\mathrm{T}} \frac{\mathrm{E}}{\mathrm{T}^2}d\mathrm{T} + i \quad . \quad . \quad [331]$$

where $\mathrm{E} = \int_0^{\mathrm{T}} \mathrm{C}d\mathrm{T}$ is the energy of the condensed phase, which may be calculated from specific heat measurements, since $\mathrm{C} = 0$ when $\mathrm{T} = 0$.[1]

120. Chemical Equilibrium in Gaseous Systems.—Consider the chemical reaction:

$$n_1\mathrm{A}_1 + n_2\mathrm{A}_2 + \ldots = n_1'\mathrm{A}_1' + n_2'\mathrm{A}_2' + \ldots$$

in which all the substances are gaseous. Let:

$$K = 1/\mathrm{K} = c_1^{n_1}c_2^{n_2}\ldots/c_1'^{n_1'}c_2'^{n_2'}\ldots$$

then, from [251] or [252], since $Q = -\mathrm{Q}$, and $\ln K = -\ln \mathrm{K}$:

$$Q = \mathrm{RT}^2 \,.\, d\ln K/d\mathrm{T}.$$

Let $\quad Q = Q_0 + a\mathrm{T} + \beta\mathrm{T}^2 + \gamma\mathrm{T}^3 + \ldots$

$$\therefore \quad d\ln K/d\mathrm{T} = Q_0/\mathrm{RT}^2 + a/\mathrm{RT} + \beta/\mathrm{R} + \gamma\mathrm{T}/\mathrm{R} + \ldots$$

$$\therefore \quad \boldsymbol{\ln K = -Q_0/\mathrm{RT} + \alpha\ln \mathrm{T}/\mathrm{R} + \beta\mathrm{T}/\mathrm{R} + \gamma\mathrm{T}^2/2\mathrm{R} + \ldots + \mathrm{I}} \quad . \quad . \quad . \quad \mathbf{[332]}$$

where I is the constant of integration (cf. § 115).

If we can find I we can determine K from purely thermal data, viz., Q_0, a, β, etc.

Suppose the reaction takes place between *solids*:

$$n_1a_1 + n_2a_2 + \ldots = n_1'a_1' + n_2'a_2' + \ldots$$

This may be effected by evaporating the requisite amounts of the solids (a_1, etc.) under their vapour pressures, allowing the reaction to proceed between the vapours with the aid of the equilibrium box, as explained in § 81, and finally condensing the vapours of the products on the solids a_1' etc. under their vapour pressures. The *affinity* of this reaction is [240]:

$$\mathrm{A}' = -\mathrm{RT}(\ln K - \Sigma n_1 \ln C_1)$$

where $\Sigma n_1 \ln C_1 = n_1 \ln C_1 + n_2 \ln C_2 + \ldots - (n_1' \ln C_1' + n_2' \ln C_2' + \ldots)$.

We may substitute $\ln C_1$, etc., from [327], and $\ln K$ from [332]:

$$\mathrm{A}' = -\mathrm{RT}[-Q_0/\mathrm{RT} + a\ln \mathrm{T}/\mathrm{R} + \beta\mathrm{T}/\mathrm{R} + \ldots + \mathrm{I} - \Sigma n_1\{-\lambda_0/\mathrm{RT} + (a_0/\mathrm{R} - 1)\ln \mathrm{T} + \beta_0\mathrm{T}/\mathrm{R} + \ldots + i_1'\}].$$

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[1] See Mündel, *Z. p. C.*, 1913, **85** 435; Crommelin, *A. A.*, 1914, **17**, 275.

Since this is ultimately a reaction between *solids*, it follows from (321) that the coefficient of T must vanish; hence:

$$\mathrm{I} - \Sigma n_1 i_1' = 0 \quad \therefore \quad \mathrm{I} = \Sigma n_1 i_1' \quad . \quad . \quad [333]$$

giving the important integration constant I in terms of the vapour pressure curves of the *pure* substances (by [326] and [331]), which may be determined once for all, and then serve for the calculation of chemical equilibria *at all temperatures*.

121. Heterogeneous Reactions.—Suppose some substances taking part in the reaction are solid. Assume first that all the substances are gaseous, and from the equation:

$$\ln K = -Q_0/\mathrm{RT} + a/\mathrm{R}\,.\ln \mathrm{T} + \beta/\mathrm{R}\,.\,\mathrm{T} + \ldots + \Sigma n_1 i_1' \ldots \quad [334]$$

subtract one after the other the expressions for the concentrations of the vapours of the solids, *e.g.* from [327]:

$$n \ln C = n\left[-\frac{\lambda_0}{\mathrm{RT}} + \left(\frac{a_0}{\mathrm{R}} - 1\right)\ln \mathrm{T} + \frac{\beta_0 \mathrm{T}}{\mathrm{R}} + \ . \ . \ . + i'\right]$$

Equation [334] will now refer to a *homogeneous* gaseous system, since all the terms relating to the solids have disappeared from ln *K* and $\Sigma n_1 i_1'$, whilst the thermal terms combine to give those which apply to the actual reaction involving the solids, because

$$(\mathrm{Q}_0 + a\mathrm{T} + \beta\mathrm{T}^2 + \ . \ . \ .) - \Sigma n\,(\lambda_0 + a_0\mathrm{T} + \beta_0\mathrm{T}^2 + \ . \ . \ .)$$

is the heat of reaction in the heterogeneous system.[1] In the application to heterogeneous reactions, therefore, the terms relating to the solids are omitted from the expressions for ln *K* and $\Sigma n_1 i_1'$.

122. The Chemical Constants.—The value of i in equation [326] may be called the (primitive) *chemical constant* of the substance. Since the data for the calculation of these (mainly vapour pressures and specific heats) are imperfectly known, Nernst adopted an empirical method for this purpose. In the equation (§ 119): $d\lambda/d\mathrm{T} = \mathrm{C}_p - \mathrm{C}$, it is known that at ordinary and higher temperatures, $\mathrm{C} > \mathrm{C}_p$, whilst at very low temperatures C approaches the limit 0 and therefore, since C_p remains finite, $\mathrm{C} < \mathrm{C}_p$. Thus at some low temperature λ must reach a maximum, and will then decrease with further rise of temperature until it becomes zero at the critical temperature, when the two phases are identical.

This behaviour may be represented approximately by the *empirical* equation[2]:

$$\lambda = (\lambda_0 + 1{\cdot}75\mathrm{RT} - \epsilon\mathrm{T}^2)(1 - p/p_c) \quad . \quad . \quad (335)$$

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[1] See also Partington, "Textbook of Thermodynamics," 1913, p. 503.

[2] Cf. also Herz, *Z. E.*, 1919, **25**, 323, who gives $\mathrm{L}_{\mathrm{T}_0} = p_c\mathrm{T}_0/\mathrm{T}_c\rho_c = (2/3)\,.\,p_c/\rho_c$.

in which a and ϵ are positive constants. This exhibits a maximum and vanishes when $p = p_c$. From (79) and the empirical equation : $p\,(V_g - V_l) = \mathrm{R}\mathrm{T}\,(1 - p/p_c)$,[1] deduced by Nernst from the measurements of Young on fluorobenzene,[2] we find :

$$\lambda = \mathrm{RT}^2 \frac{d \ln p}{d\mathrm{T}} (1 - p/p_c) \quad . \quad . \quad . \quad . \quad (335a)$$

and, by substitution of λ from equation (335) and integration :

$$\ln p = -\frac{\lambda_0}{\mathrm{RT}} + 1{\cdot}75 \ln \mathrm{T} - \frac{\epsilon}{\mathrm{R}} \mathrm{T} + i \quad . \quad . \quad (336)$$

where i is the constant of integration or,[3]

$$\log \mathrm{p} = \frac{-\lambda_0}{4{\cdot}576\mathrm{T}} + 1{\cdot}75 \log \mathrm{T} - \frac{\epsilon}{4{\cdot}576} \mathrm{T} + C \quad . \quad (336a)$$

where C is called by Nernst the *conventional chemical constant.*[4]

The formula (336a) contains only three constants (λ_0, ϵ, C), but " in numerous cases has been found to reproduce with considerable accuracy the vapour pressure curves of crystals and liquids over enormous ranges of temperature." [5] Mündel has shown, however, that for organic substances of high molecular weight the values of λ_0, ϵ, and C may be varied within certain limits without affecting the agreements of the formula with the experimental data, " which, naturally, affects the certainty of the determinations of C " made in this way. Also, at very low temperatures equation (336) does not pass into (329); the term in ln T remains 1·75 ln T instead of 2·5 ln T, which appears to be the correct value at very low temperatures.

Equation (335a) may be improved by using Berthelot's characteristic equation instead of Young's : one then finds [6] :

$$\lambda = \mathrm{RT}^2 \frac{d \ln p}{d\mathrm{T}} \left[1 + \frac{9}{128} \pi\tau(1 - 6\tau^2) - \frac{v_l}{v_g} \right] \quad . \quad . \quad (335b)$$

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[1] This is compatible with Berthelot's equation (131 of § 51), since in the region contemplated, $1/\tau = 0{\cdot}65$ to $0{\cdot}70$, hence the value of the correction term $\frac{9}{128}(1 - 6\tau^2)$ is nearly -1. Cf. F. Russ, *Z. p. C.*, 1913, **82**, 221.

[2] Nernst, " Theoretische Chemie," 8–10 Aufl., 1921, p. 796 ; " Grundlagen," p. 109.

[3] Cf. Herz, *Z. E.*, 1919, **25**, 323.

[4] Cf. Grassi, *N. C.*, 1914, **7**, i., 313.

[5] Nernst, *D. p. G.*, 1909, **11**, 313, 336 ; Weber, *Kongelige Danske Videnskabernes Selskabs*, 1915, p. 459 ; Siemens, *A. P.*, 1913, **42**, 871 ; Mündel, *Z. p. C.*, 1913, **85**, 435 ; U. Grassi, *N. C.*, 1914, **7**, 313 ; Sonaglia, *ibid.*, 321 ; C. A. Crommelin, *A. A.*, 1913, **16**, 477 (vapour pressure of solid and liquid argon to – 206° C.) ; Kohner and Winternitz, *P. Z.*, 1914, **15**, 393 ; Ariès, *C. R.*, 1917, **164**, 343.

[6] Nernst, *Z. E.*, 1916, **22**, 185 ; cf. Leduc, *C. R.*, 1913, **156**. 225 ; Gay, *C. R.*, 1913, **156**, 1464.

The following table, given by Siemens (*loc. cit.*), shows the values found :

Substance.	T.	λ calcd. cal.		λ obs. cal.
		(335a).	(335b).	
CS_2 . .	287·2	6743	6667	6614
CO_2 . .	194·7	6011	5929	6626
O_2 . .	90·1	1624	1583	1629
O_2 . .	68·2	1784	1776	1777
N_2 . .	77·2	1386	1327	1335
N_2 . .	63·2	1459	1446	1450

According to Cederberg:

$$C = 1{\cdot}6 \log p_c \quad . \; . \; . \; . \; . \; . \; . \quad (337)$$

For most substances the value $C = 3$ is sufficiently accurate, as is seen from the table of chemical constants given below. By comparison of (336a) and (326) it is seen that :

$$C = i/2{\cdot}3023 \quad . \; . \; . \; . \; . \; . \; . \quad (338)$$

The following table of conventional chemical constants is given by Nernst :

He	0·6	HI	3·4	H_2O . . .	3·6
H_2	1·6	NO	3·5	CCl_4. . .	3·1
CH_4. . . .	2·5	N_2O . . .	3·3	$CHCl_3$ . .	3·2
N_2	2·6	H_2S. . .	3·0	C_6H_6 . .	3·0
O_2	2·8	SO_2. . .	3·3	C_2H_5OH . .	4·1
CO	3·5	CO_2. . .	3·2	$(C_2H_5)_2O$ . .	3·3
Cl_2	3·1	CS_2 . . .	3·1	Acetone . .	3·7
I_2	3·9	NH_3 . . .	3·3	Propyl acetate .	3·8
HCl. . . .	3·0				

Other formulæ (" purely accidental," according to Nernst) for the chemical constant are: $C = 1{\cdot}1a = 0{\cdot}14\lambda\,/T_B$, where a is the constant of van der Waals' vapour pressure formula (§ 40) ; λ_e is the molecular heat of evaporation, and T_B the absolute boiling point.[1]

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[1] A relation between the critical data and the chemical constant has also been deduced by Henglein (*Z. an. C.*, 1920, **114**, 234 ; *Z. p. C.*, 1921, **98**, 1). The chemical constant is calculated by the equation $C = \lambda_0/4{\cdot}571T$, where $\lambda = (\lambda_0 + AT - BT^2 - \ldots)(1 - p/p_c)$ is the latent heat and p_c, T_c are the critical constants. Nernst's equation, $C = 0{\cdot}14\lambda/T_B$, where T_B is the absolute boiling point, follows from van der Waals' equation, $\log p/p_c = a(1 - T_c/T)$. Cederberg's equation, $C = k \log p_c$ (where k is 1·6 in many cases), also follows from this equation, since it is a special case of the more general equation, $C = 1{\cdot}1 \log p_c(T_c/T_B - 1)$.

Nernst[1] observes that in the applications the chemical constant C always appears in the equations together with the term $1{\cdot}75 \log T$, and since the factor 1·75 is empirical [and probably incorrect] the two must be used together. When different values are used instead of 1·75, different values of C must also be used to obtain agreement, and a great part of the comparison with experimental results therefore rests on a somewhat tentative foundation.

The calculation of the (primitive) chemical constant i from the quantum theory (see § 139), which is free from doubt in the case of monatomic gases, is therefore a useful check on this part of the theory. The values so obtained are not, as would be expected, the same as those found by the empirical method used by Nernst. The formula given by the quantum theory is:

$$C = -1{\cdot}589 + 1{\cdot}5 \log M,$$

where M is the atomic weight of the substance. The following table gives the results so far obtained in this direction[2]:

	M.	C obs.	C calc.
H_2[3] . .	2·016 ...	$-1{\cdot}23 \pm 0{\cdot}15$ ...	$-1{\cdot}13$
A . .	39·88 ...	$0{\cdot}75 \pm 0{\cdot}06$ ...	0·81
Hg . .	200·6 ...	$1{\cdot}83 \pm 0{\cdot}03$ ...	1·86
Zn . .	65·37 ...	$1{\cdot}23 \pm 0{\cdot}26$ ...	1·13
Cd . .	112·4 ...	$1{\cdot}65 \pm 0{\cdot}31$ ...	1·49

Further progress in the *strict* evaluation of chemical constants must be based, as Nernst[4] points out, on (330), the general integral of the vapour pressure equation, which appears first to have been given by the author.[5] This presupposes, however, a knowledge, which we do not at present possess, of the vapour pressure curves and specific heats of substances.[6]

123. Examples of the Application of Nernst's Theorem.—*Gaseous Equilibria.*—If the equilibrium is specified in terms of the *partial pressures* (§ 84), and if (following Nernst's notation) we put:

$$K' = 1/K' = p_1^{n_1} p_2^{n_2} \ldots / p_1'^{n_1'} p_2'^{n_2'} \ldots = K(RT)^{n_1+n_2+\ldots-n_1'-n_2'\ldots}$$

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[1] "Lehrbuch," 8–10 Aufl., pp. 799, 805.

[2] Nernst, "Grundlagen des neuen Wärmesatzes," 1918, pp. 143 ff. (H_2, A, Hg); Egerton, *P. M.*, 1920, **39**, 1 (Zn, Cd, Hg). The errors in the cases of Zn and Cd are too large to enable any definite conclusion to be drawn. Cf. also Lindemann, *P. M.*, 1920, **39**, 21; Ladenburg and Minkowski, *Z. P.*, 1921, **8**, 137.

[3] Cf. Kohner and Winternitz, *P. Z.*, 1914, **15**, 393, 645.

[4] "Lehrbuch," p. 807.

[5] "A Textbook of Thermodynamics," 1913, p. 493, equation (7).

[6] Cf. Langen, *Z. E.*, 1919, **25**, 25; Herzfeld, *A. P.*, 1916, **51**, 261; Eggert, *P. Z.*, 1919, **20**, 570. On chemical constants and entropy of gases, see Njegovan, *Z. p. C.*, 1918, **92**, 275.

and if the heat of reaction is expressed in the form:

$$Q_p = Q_0 + 3{\cdot}75\Sigma n_1 T + \Sigma n_1 \beta \,.\, T^2$$

from (38b) and the assumption of § 122, then:

$$\log K' = -Q_0/4{\cdot}576T + 1{\cdot}75\Sigma n_1 \,.\, \log T + \Sigma n_1 \beta T/4{\cdot}576 + \Sigma n_1 C_1 \quad . \quad . \quad [339]$$

As an example of the application of this equation Nernst [1] considers the dissociation of water vapour, but instead of calculating the extent of dissociation at a given temperature he calculates the temperature corresponding with a given dissociation, which is much less influenced by deviations between calculation and experiment. A similar procedure is adopted in his monograph.[2] The true molecular heats at constant pressure from Pier's researches are:

$$H_2\ 6{\cdot}685 + 9 \,.\, 10^{-4}\theta;\ O_2\ 6{\cdot}885 + 9 \,.\, 10^{-4}\theta$$

$$H_2O\ 8{\cdot}050 + 10 \,.\, 10^{-4}\theta + 8 \,.\, 10^{-10}\theta^3$$

and the heat of formation of $2H_2O$ is then:

$$Q_p = 115{,}090 + 4{\cdot}155\theta + 3{\cdot}55 \,.\, 10^{-4}\theta^2 - 4 \,.\, 10^{-10}\theta^4.$$

In order to use the values of the conventional chemical constants in § 122, however, Q_p must be expressed in the form:

$$Q_p = Q_0 + \Sigma n_1 \,.\, 3{\cdot}5T + \Sigma n_1 \beta \,.\, T^2 + \text{etc.}$$

and the above equation is altered by trial until the form:

$$Q_p = 113{,}900 + 3{\cdot}5\,T + 2{\cdot}2 \,.\, 10^{-3}T^2 - 1{\cdot}1 \,.\, 10^{-6}T^3 - 9 \,.\, 10^{-11}T^4$$

is obtained, which gives:

$$\log K' = -\frac{113{,}900}{4{\cdot}576T} + 1{\cdot}75 \log T + \frac{2{\cdot}2 \,.\, 10^{-3}}{4{\cdot}576}T - \frac{1}{2} \,.\, \frac{1{\cdot}1 \,.\, 10^{-6}}{4{\cdot}576}T^2 - \frac{1}{3} \,.\, \frac{9 \,.\, 10^{-11}}{4{\cdot}576}T^3 + \Sigma n_1 C_1.$$

From the table of chemical constants: $\Sigma n_1 C_1 = 2 \times 1{\cdot}6 + 2{\cdot}8 - 2 \times 3{\cdot}6 = -1{\cdot}2$.

When the values of K' found experimentally are inserted in the equation one finds: [3]

100 x obs.		log K' obs.		T obs.		T calc.
0·0197	...	− 12·026	...	1500	...	1486
1·18	...	− 6·687	...	2155	...	2131
1·77	...	− 6·159	...	2257	...	2226

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[1] "Lehrbuch," 8–10 Aufl., p. 799.

[2] "Applications of Thermodynamics to Chemistry," 1907.

[3] Jellinek, "Gasreaktionen," p. 675. Many other examples will be found in this treatise.

In the present state of this part of thermodynamics it is probably quite sufficient to omit the term in β in [339], and to put $Q_0 = Q_p$, the heat of reaction at constant pressure as given in the thermochemical tables. The *approximate* equation :

$$\log K' = -Q_p/4{\cdot}576T + 1{\cdot}75\Sigma n_1 \,.\, \log T + \Sigma n_1 C_1 \quad . \; . \; . \; . \; . \; . \quad [340]$$

will then be a useful guide in a large number of technical and laboratory problems in cases where, for lack of data (mainly specific heats), the more exact equations cannot be used. Two examples may be given for the purpose of illustration.

The reduction of carbon dioxide by carbon : [1]

$$2CO \rightleftharpoons CO_2 + C + 39{,}300 \text{ cal.}$$

In accordance with § 121 the constants referring to the solid carbon do not enter either log K' or $\Sigma n_1 C_1$. The approximate equation [340] gives for 800° C. :

$$\log p_{CO}{}^2/p_{CO_2} = -39{,}300/4{\cdot}576 . 1073 + 1{\cdot}75 \log 1073 + (2 \times 3{\cdot}5 - 3{\cdot}2)$$
$$= -8{\cdot}004 + 5{\cdot}304 + 3{\cdot}8 = 1{\cdot}1,$$
$$\therefore\ 1/K' = p_{CO_2}/p_{CO}{}^2 = 0{\cdot}0794.$$

Boudouard found at this temperature 7 per cent. of CO_2 in the gas,

$$\therefore\ 1/K' = 0{\cdot}07/(0{\cdot}93)^2 = 0{\cdot}0809.$$

The good agreement in this case is probably accidental.[2]

Dissociation of metallic oxides.—Stahl [3] calculated the temperatures at which the pressure of oxygen over dissociating metallic oxides reaches 0·21 atm. (when they have a dissociation pressure equal to the partial pressure of oxygen in the atmosphere) from the equation:

$$2MO \rightleftharpoons 2M + O_2$$

$\log 0{\cdot}21 = -0{\cdot}6778 = -Q/4{\cdot}576T + 1{\cdot}75 \log T + 2{\cdot}8$, in which $2{\cdot}8$ = chemical constant of oxygen. The values of log p are plotted against T and cut by the ordinate $\log p = -0{\cdot}6778$ to find the required temperatures. Q is twice the heat of formation of the oxide.

Dissociation of ammonium hydrosulphide :

$$NH_4HS \rightleftharpoons H_2S + NH_3.$$

Molecular heats: solid NH_4HS, 19·1; gaseous NH_3, 9·5;

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[1] Greenwood, "Industrial Gases," 1920, p. 14.

[2] See Jellinek and Diethelm, *Z. an. C.*, 1922, **124**, 203. Instead of 3·8, the integration constant is found to be 3·876. Other examples will be found in the monographs of Nernst cited. Cf. also Stern, *A. P.*, 1914, **44**, 497.

[3] *Metallurgie* (Halle), 1907, p. 682.

gaseous H_2S, 8·5. Heat of dissociation of NH_4HS, 22,800 gm. cal. (All these values refer to T = 300)

$$\therefore Q_p = 21{,}900 + 7{\cdot}07T - 0{\cdot}013T^2$$

$$\therefore \tfrac{1}{2}\log K' = \log(p/2) = -2396/T + 1{\cdot}75\log T - 0{\cdot}0014T + 3{\cdot}15,$$

where 3·15 = mean of chemical constants for NH_3 and H_2S. For T = 298·1, $p = 0{\cdot}661$ atm. (obs.). If we put $p = 0{\cdot}661$ in the above equation we find T = 318. The approximate equation :

$$\log(p/2) = -11{,}400/4{\cdot}576T + 1{\cdot}75\log T + 3{\cdot}15$$

gives T = 311.

The calculation of the E.M.F. of a gas cell may be carried out by combining [339] and [309].[1] In the case of the oxy-hydrogen cell, [309] gives $E = \frac{0{\cdot}0001984}{4}\log\frac{1}{K'\pi^2}$, where $\pi = 0{\cdot}0191$ atm. = vap. press. of water at 17° C. The value of log K' is calculated for T = 290 as explained above, and the value of E is then found to be 1·237 volts, in good agreement with the observed value.[2]

A consideration of [340] shows that, when $\Sigma n_1 = 0$, and $\Sigma n_1 C_1 = 0$ (similar substances), then if $Q = 0$ (transformation of optical isomers), $K' = 1$ exactly. If Q is approximately zero, K' is approximately 1, *i.e.*, *all* the components are present in appreciable amounts (*e.g.*, $H_2 + I_2 \rightleftarrows 2HI$). But if Q is positive and appreciable, then at low temperatures log K' is strongly negative, *i.e.*, the reaction is practically complete (*e.g.*, $H_2 + Cl_2 = 2HCl$). If Q is negative under the same conditions (*e.g.*, $N_2 + O_2 = 2NO$; $2C + H_2 = C_2H_2$), the compounds are formed in appreciable amounts only at high temperatures. In cases where $\Sigma n_1 \neq 0$ the sign and magnitude of the heat of reaction is important, *e.g.*,

$$2NO_2 = N_2O_4 + 12{,}500 \text{ cal.}$$

At T = 300 the dissociation is appreciable, and at slightly higher temperatures is nearly complete.

In the reaction $CaO + CO_2 = CaCO_3 + 42{,}520$ cal.,[3] we take $C_{CO_2} = 3{\cdot}2$

$$\therefore \log p = -42{,}520/4{\cdot}576T + 1{\cdot}75\log T + 3{\cdot}2 ;$$

or, if $T = T_1$ when $p = 1$ atm.

$$Q/4{\cdot}576T_1 = 1{\cdot}75\log T_1 + 3{\cdot}2 \quad . \quad . \quad . \quad . \quad [341]$$

---

[1] Cf. Nernst, *B. B.*, 1909, p. 247.

[2] Nernst, "Lehrbuch," p. 834.

[3] Cf. Mitchell, *C. S.*, 1923, **123**, 1055.

When T_1 is approximately 250 to 350, log T changes only slowly with T

$$\therefore \quad 4{\cdot}576\,(1{\cdot}75 \log T + 3{\cdot}2) = 34 \text{ approx.}$$

$$\therefore \quad Q/T_1 = 34 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (342)$$

which is the de Forcrand-Matignon rule (§ 49). This holds only under the given conditions; in other cases the more general equation [341] must be preferred.

124. Planck's Statement of Nernst's Theorem.—A rather different statement of Nernst's theorem has been advanced by Planck. This is in agreement with the quantum theory (see Chapter XVIII.) and with the experimental values of specific heats at very low temperatures (§§ 4, 131 ff).

According to Planck,[1] *the entropy of a condensed* [*solid or liquid*] *chemically homogeneous substance* [not a solution] *vanishes at the zero of absolute temperature :*

$$\mathbf{s = 0 \text{ when } T = 0} \quad . \quad . \quad . \quad . \quad \mathbf{(343)}$$

$$\text{Now } s = \int^{T} \frac{c_p}{T}\,dT \quad \therefore \quad 0 = \int^{0} \frac{c_p}{T}\,dT.$$

Both c_p and T are by nature positive, hence this result can hold only when the lower limit of the integral is 0 and it is then always true. Thus

$$\mathbf{s = \int_0^T \frac{c_p}{T}\,dT} \quad . \quad . \quad . \quad . \quad . \quad \mathbf{(343a)}$$

so that the entropy in this case has a definite absolute value. This is also required by the quantum theory. Nernst's formulation:

$$\text{Lim}\,\frac{dA}{dT} = dQ/dT = s_1 - s_2 = 0, \text{ for } T = 0 \quad . \quad . \quad (344)$$

does not involve the vanishing of s_1 and s_2 separately, but shows that the entropy is unchanged by changes in the system under the above conditions. This would indicate that the entropies of two or more forms of a substance are equal at the absolute zero.[2] G. N. Lewis and G. E. Gibson[3] consider that the entropy of a perfect crystal is zero at the absolute zero, but that of a non-crystalline form of the same substance is greater than zero, since in this case the arrangement of the parts of the system is more random than in the perfect crystal. The vanishing of the entropy of crystalline substances is regarded as established by experiment;[1] experiments with glycerol in the crystalline and glassy condition indicate that the latter has an entropy greater by 5·6 gm. cal./1° per mol. at 70° abs. than that of the crystals, and this difference probably extends to the absolute zero.[2]

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[1] "Thermodynamik," 3 Aufl., § 281 ff.; *Ber.*, 1912, **45**, 5.

[2] Entropy of solids and gases: Latimer, *J. A. C. S.*, 1921, **43**, 818; *ibid.*, 1922, **44**, 2136.

[3] *J. A. C. S.*, 1917, **39**, 2554; 1920, **42**, 1529.

Pagliani[3] calculates by (343) the entropies of elements and compounds at the melting point. The values for elements diminish as the atomic weight increases, and the entropy per gram atom of the metals before fusion is not constant, as asserted by Tammann.[4]

The relation to the statistical conception of entropy will be clear (§ 68). The entropy is a measure of the "mixed-up-ness" of the system. When the entropy is a minimum, the mixed-upness is also a minimum. Thus, when all the molecules are in the same state the entropy is a minimum. They are all in the same state of motion at the absolute zero, since then they are all at rest, *i.e.*, their kinetic energies are all equal to zero; they may have zero-energy. In the case of a substance which can exist in crystalline and amorphous forms, the latter will have more entropy than the former, in which the molecules are marshalled into order. We may, therefore, expect that the entropy of a glassy substance will not vanish even at T = 0, or that the difference of entropies of the glassy and crystalline forms will not vanish, since there is still some disordered arrangement of the molecules to be cleared up before the system can have the minimum entropy. These ideas[5] have been confirmed by experiment, as stated above.

Equation (343) shows that:

$$\text{Lim}\, c_p = 0 \quad \text{for } T = 0 \quad . \; . \; . \; . \; . \quad (345)$$

since the integral does not become infinite, but approaches the value zero. This remarkable result appears to be verified by experiment (§ 4). In the same way it can be shown that:

$$\text{Lim}\, c_v = 0 \quad \text{for } T = 0 \quad . \; . \; . \; . \; . \quad (346)$$

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[1] Lewis, Gibson, and Latimer, *J.A.C.S.*, 1922, **44**, 1008.

[2] Gibson and Giauque, *J.A.C.S.*, 1923, **45**, 93.

[3] *A. L.*, 1915, **24**, i., 835; *N. C.*, 1915, **10**, ii., 5; 1916, **11**, i., 118; cf. Lewis and Randall, "Thermodynamics," pp. 150 ff.

[4] *Z. p. C.*, 1913, **85**, 273.

[5] Partington, "Thermodynamics," 1913, p. 531.

Differentiate (343a) with respect to p:

$$\therefore \quad \int_0^T \frac{1}{T}\left(\frac{\partial c_p}{\partial p}\right)_T dT = (\partial s/\partial p)_T = -(\partial v/\partial T)_p \text{ from (184a).}$$

$$\text{But} \qquad (\partial c_p/\partial p)_T = -T(\partial^2 v/\partial T^2)_p \text{ from (52)}$$

$$\therefore \quad \text{by integration } [\partial v/\partial T]_T - [\partial v/\partial T]_{T=0} = [\partial v/\partial T]_T$$

$$\therefore \qquad \text{Lim}\,(\partial v/\partial T)_p = 0 \qquad \text{for } T = 0 \quad . \quad . \quad . \quad . \quad (347)$$

which has been confirmed indirectly by experiment.[1]

General Statement of Nernst's Theorem.—Nernst has shown that the content of his principle may be stated in a form analogous to the two laws of thermodynamics:

It is impossible by means of any finite process to cool a body to the absolute zero.

On the assumption that all the specific heats are vanishingly small at the absolute zero, the theorem in the usual form (321) follows from the above statement.[2]

Berthelot[3] had already pointed out that, if the heat capacities are regarded as constant, the entropy in the vicinity of the absolute zero tends to the value $-\infty$, " which shows that the calculations then lose all physical or chemical significance." He also[4] adopted " the hypothesis " that $T(S_2 - S_1)$ is zero at the absolute zero, in which case the heat evolution would be equal to the affinity. Stern[5] concludes that the entropy of solid solutions also converges to a zero value with falling temperature.

125. Results of Thermodynamics.—The results of pure thermodynamics are founded on two very general laws derived from common experience, viz., the First and Second Laws of Thermodynamics. The validity of these laws would now hardly be questioned by a person of intelligence, even though he knew nothing of scientific methods. The first asserts that a machine cannot go on furnishing work from nothing, the second that a machine cannot go on working without fuel at the expense of the surrounding heat. In the validity of their application, under proper conditions, we may therefore have implicit confidence. It is not to be anticipated that the general conclusions which depend on these two laws alone will suffer serious modifications. In this respect they differ from results derived from kinetic or molecular theories. These set out from assumptions which are so far from obvious that it is only with difficulty that they can be apprehended by serious students of science, they are liable to modification with the further progress of scientific investigation, and there is no general agreement as to their interpretation.

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[1] Grüneisen, *A. P.*, 1908, **26**, 211; and C. L. Lindemann, *P. Z.*, 1911, **12**, 1197.

[2] Nernst, " Grundlagen des neuen Wärmesatzes," pp. 72 ff.; Jellinek, " Physikalische Chemie der Gasreaktionen," pp. 467 ff.

[3] " Thermochimie," I., 16.

[4] *Ibid.*, p. 17.

[5] *A. P.*, 1916, **49**, 823.

In the application of the laws of thermodynamics, or consequences derived *directly* from them, such as the relation $(Q_1 - Q_2)/Q_1 = (T_1 - T_2)/T_1$, to actual systems, it is necessary to introduce assumptions, some of which may be based on experimental results, and some on particular theories. Such are the laws of ideal gases, and the assumptions relating to dilute solutions. The results then obtained, such as the Law of Mass Action, are not based simply on the laws of thermodynamics, and they may be true or not according as the assumptions introduced are correct or false. It may happen that the results are true even though the assumptions are incorrect, since errors may compensate, or incorrect assumptions give the same results as correct ones. We must guard against the error of supposing, because a result derived by means of thermodynamics from some particular assumptions happens to agree with some actual cases, that these assumptions are "proved" by the laws of thermodynamics. This cannot be the case.

Thermodynamics enables us to deduce a great number of useful relations without special knowledge of the structure of matter. Conversely, it cannot tell us anything about the structure of matter, or if it does, it is only because we have made some assumptions foreign to thermodynamics. Systems of "molecular thermodynamics" must be looked upon with suspicion. There are two schools of thought, for example, one believing that the law of mass action applies to electrolytes and the other that it does not. Both have brought forward arguments alleged to rest on the foundations of thermodynamics, and that science has, therefore, appeared to have been capable of reaching contradictory conclusions. This is only because we cannot get out of any method of reasoning more than we put in. If we put in contradictory hypotheses we can get out contradictory results, and if we put in a suitable hypothesis we can "prove" anything on earth.

We must also beware of assuming, because thermodynamics can reach results which follow also from atomic theories, that the latter are superfluous. For the results obtained with the assistance of thermodynamics come from experimental data, whilst atomic theories can often give the same results without any experimental facts at all. They can also lead us very much further in some directions than thermodynamics, although the conclusions may be less certain.

EXAMPLES XVII.

1. By means of Nernst's equations $Q = Q_0 + \beta/2 \,.\, T^2 + \gamma/3 \,.\, T^3$ and $A = Q_0 - \beta/2 \,.\, T^2 - \gamma/6 \,.\, T^3$, find the free energy change of the conversion of supercooled water into ice at — 5° C. and — 20° C. The latent heat of water at 0° C. = 80 cals., and the difference between the specific heats of water and ice at 0° C. = 0·498.

2. The heat of the reaction $N_2 + O_2 = 2NO$ is 43200 cals. (absorbed). By means of Nernst's heat theorem show that the maximum amount of NO formed in air at 1800° K. is about 0·1% (Nernst).

3. The heat of dissociation of $2CO_2$ into $2CO + O_2$ is 136,000 cals. Calculate the degree of dissociation at 2000° C. and 1 atm. pressure.

4. For solid iodine the constants in Nernst's equation (336b) are $\lambda_0 = 14{,}609$, $\epsilon = 0{\cdot}0143$, $C = 4{\cdot}0$; calculate the vapour pressure of solid iodine at 10° C.

5. The heat of the reaction $H_2 + S$ (solid) $= H_2S$ is very approximately 5000 cals. evolved. C, the chemical constant for H_2, is approx. 1·6 and for H_2S, 3·0. Show that the logarithm of the equilibrium constant is given by the approximate expression — 1092/T — 1·4.

6. The heat of combination of 2 mols H_2 and 1 mol O_2 to form $2H_2O$ (vapour) is 115,160 gm. cals. The chemical constants of the substances concerned are H_2 1·6; O_2 2·8; H_2O (steam) 3·6. Find an expression connecting the degree of dissociation with the temperature when (*a*) the pressure is 1 atm., and (*b*) the pressure is 2 atm.

Calculate from the formula the percentage dissociation at the following temperatures ($p = 1$ atm.), comparing the values obtained with those given:

$T =$	1300	1500	1705	2257° K.
$100x =$	0·0027	0·0197	0·102	1·77

What is the probable cause of the discrepancy between the observed and calculated values ?

7. The heat of transition of the reaction Sn (white)⟶Sn (grey) is given by the following equation, which only holds from T = 80° K. to T = 292° K.:
$Q(\text{evolved}) = 332{\cdot}4 + 1{\cdot}365\,T - 4{\cdot}37\,.\,10^{-3}T^2 + 9{\cdot}72\,.\,10^{-6}T^3 - 8{\cdot}1\,.\,10^{-9}T^4$.
The transition point is 19° C. ($p = 1$ atm.). Plot Q against T and, using the same axes, plot A, the affinity, against T. Compare the graph with Fig. 42 in the text. Produce the curves to show that they approach asymptotically in the neighbourhood of T = 0° K.

8. According to Thomsen the heat of dissociation of strontium carbonate is 55,770 cals. per mol, absorbed, the pressure being 1 atm. Calculate the temperature at which the dissociation pressure is 1 atm.

9. Find at what temperature $MnCO_3$ is completely dissociated under atmospheric pressure if the heat of dissociation of this substance is 23,500 cals. per mol.

10. Find the E.M.F. of the cell $Ag/AgI/I_2$ at 18° C., all the components being solids, from the following data: heat of formation of AgI from its

elements, 13,800 cals. per mol (Thomsen); specific heats: AgI = 0·057, Ag = 0·056, I_2 = 0·054; atomic weights, Ag = 107·88, I_2 = 126·92.

11. The molecular heat of ice is given by the equation $C = 3{\cdot}0 + 0{\cdot}0223T$ and its molar heat of fusion is 1440 cals., this number increasing 9 units per 1° rise in temperature. Find the maximum work of the reaction $CuSO_4 + H_2O$ (ice) = $CuSO_4,H_2O$ at 18° C., given that the heat capacity of the water of crystallisation = 6·99 cals. per mol, and the heat of hydration of anhydrous $CuSO_4$ by liquid water = 6460 cals. per mol at 18° C.

(N.B.—It is necessary to give the data for water of crystallisation in terms of ice, as the specific heat of water varies irregularly with temperature.)

12. With the help of some of the data in the preceding question calculate an expression for the maximum work of hydration of K_4FeCy_6 to the trihydrate $K_4FeCy_6,3H_2O$ given (i.) the total heat capacity of the water of crystallisation = 11·75 cals. at 9° C., (ii.) the heat of hydration per mol of salt by liquid water = 1630 cals. at 18° C.

13. By means of [340] show that the heat of dissociation of N_2O_4 is approximately 12,400 cals. per mol (absorbed), given that the degrees of dissociation are 0·1996 and 0·9267 at temperatures 299·7° K. and 384·3° K. respectively (p = 1 atm.).

CHAPTER XVIII

The Quantum Theory

126. Specific Heats of Gases: Dynamical Theory.—The fundamental equation of the kinetic theory of ideal gases is:

$$pv = mG^2/3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad [348]$$

where p = pressure, v = volume, m = mass, of the gas, and G^2 is the mean square velocity of translation of the molecules.[1]

For unit mass, v = specific volume = 1/density = $1/\rho$:

$$\therefore \qquad pv = G^2/3 \qquad \text{or } p = \rho G^2/3 \quad . \quad . \quad . \quad . \quad . \quad [349]$$

The kinetic energy of translation of all the molecules is equal to $G^2/2$ per unit mass, or, from [349], to $3/2 . pv = 3RT/2M$, and the kinetic energy of translation per mol is:

$$U = MG^2/2 = 3RT/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad [350]$$

The molecular heat at constant volume, on the assumption that all the energy is translational will be:

$$C_v = (\partial U/\partial T)_v = 3R/2 = 1{\cdot}5 \times 1{\cdot}987 = 2{\cdot}980 \text{ gm. cal.}$$

Thus: $\gamma = C_p/C_v = (C_v + R)/C_v = (2{\cdot}98 + 1{\cdot}987)/2{\cdot}98 = 1{\cdot}667$.

These values are found for monatomic gases such as argon, helium, and mercury vapour, and are independent of temperature up to 3000° K. In the case of helium, the value of γ is given by Scheel and Heuse [2] as 1·660 at 18° C. and 1·673 at − 180° C., indicating possibly a slight decrease of C_v at very low temperatures.

In the case of gases containing more than one atom in the molecule, the value of C_v is always greater than 2·98; it increases with the complexity of the molecule,[3] and also with the temperature.

127. Boltzmann's Theory of the Energies of Gas Molecules.—The dependence of molecular heat on molecular complexity was explained by Boltzmann [4] by *energy of rotation*, in addition to the translational kinetic energy of [350]. In a monatomic gas rotational energy is absent or constant; if the centre of gravity of the *smooth* atom corresponds with the geometrical centre of a sphere, no change of rotational energy can be caused by collisions. But in a diatomic gas the two atoms may be regarded as massive particles rigidly attached a fixed distance apart, and the rotation of this dumb-bell structure can be resolved in two perpendicular planes. Rotation about the molecular axis will be absent or constant, since the molecule is symmetrical about this axis, and no change in this part of the energy can be brought about by collisions. The distribution of the energy among the degrees of freedom (f) of such a system is given by *Maxwell's Equipartition Law: the kinetic energy is equally shared among all the degrees of freedom.* The total energy of a monatomic molecule is 3/2 . RT per mol, and this is divided among three degrees of freedom of translational motion, hence the share per degree of freedom is RT/2 per mol, or kT/2 per molecule, where $k = R/N_0$, N_0 being *Avogadro's constant*, or the number of molecules in one gram molecule or mol. The latest determinations (§ 138) give $N_0 = 6{\cdot}06 \times 10^{23}$, $R = 8{\cdot}315 \times 10^7$ ergs/1°, $\therefore\ k = 1{\cdot}37 \times 10^{-16}$ ergs/1° C. (*Boltzmann's constant*).[1]

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[1] See the author's "Inorganic Chemistry," chap. xv.

[2] *A. P.*, 1912, **37**, 79; 1913, **40**, 473; *Z. E.*, 1913, **19**, 593.

[3] Cf. the interesting calculations of Berthelot, "Thermochimie," I., 47 ff.

[4] "Gastheorie," II., p. 128.

For the diatomic dumb-bell molecule, the total kinetic energy will be 3/2 . RT for the three translational degrees of freedom, and 2/2 . RT for the two rotational degrees of freedom, or 5/2 . RT, per mol, in all. Thus, $C_v = 5/2 . R = 4{\cdot}97$ gm. cal. Also, $C_p = 4{\cdot}97 + 1{\cdot}99 = 6{\cdot}96$, and $\gamma = C_p/C_v = 1{\cdot}40$.

Diatomic Molecules.—The experimental values show that diatomic gases fall into three groups:[2] (*a*) One gas, hydrogen, having C_v appreciably lower than the equipartition value ($f = 5$; $C_v = 4{\cdot}97$) corresponding with a rigid symmetrical molecule. C_v diminishes with temperature fairly rapidly from 4·87 at 0° C. to 2·98 at − 200° C., remaining at the latter value to the lowest temperatures investigated (*c.* 30° K.). (*b*) A group of diatomic gases, including oxygen, nitrogen, carbon monoxide, nitric oxide, and halogen hydracids, for which C_v at ordinary temperatures is almost exactly the equipartition value and is constant over a fairly wide range of temperature. The different members of this group, however, exhibit small but well-established differences in C_v (see tables below). (*c*) The free halogens, Cl_2, Br_2, and I_2, have appreciably higher values of C_v, approximating to 6 at ordinary temperatures, but dependent on temperature.[1] This gives $f = 6$. The case of hydrogen cannot be explained on the theory of equipartition.

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[1] The above values refer to the atomic weight standard O = 16·00; k is independent of this.

[2] Partington, *F. S.*, 1922, 17, 734.

It is convenient to call the difference between C_v and 2·98, the translational energy, the *internal energy* of a molecule. In the normal diatomic gases $C_v^{\text{int}} = 1{\cdot}987$ cal. might also be explained by assuming that the molecule as a whole had no rotation, but that the two atoms were oscillating in the line of the axis. This appears less probable for at least two reasons: (i.) It is difficult to explain the absence of rotations. (ii.) The difference between molecules of types (*b*) and (*c*).

The effect of the introduction of a second halogen atom into a molecule, as exemplified by the types HX and X_2, and in organic derivatives, is of interest.[2]

Polyatomic Molecules.—The data in this field are very incomplete, and the values of C_v depend on temperature in a manner which, although more marked than in the case of diatomic molecules, is even less accurately known. The following are typical results.

Gas.	Temperature C.	C_v.	f_i (Internal).
CO_2	17	6·76	3·78
SO_2	13	7·27	4·29
NH_3	14·5	6·71	3·73
N_2O	12	6·76	3·78

CO_2 and N_2O have practically identical molecular heats. If the values of f_i are diminished by 2·98, the *rotational* part, the remainder may be taken as a measure of the *residual energy*, which appears to run parallel with the activities of the molecules.[3]

The variability of specific heat with temperature is not a fatal objection to the theory of equipartition. The number of degrees of freedom is variable only in whole multiples for each individual molecule, but in the gas as a whole there may be molecules with different numbers of degrees of freedom, and in the gas there is always a fraction of the molecules with energies above the average. The number of degrees of freedom may, *for the gas as a whole*, be treated as continuously variable with temperature.

A detailed investigation [4] shows that with a theoretical value of df/dT, the experimental results to the lowest temperatures may be covered without recourse to the quantum theory. In this case, however, it is necessary to assume $f_0 = 3$ for the diatomic gas hydrogen, a result difficult to interpret (since it corresponds with the translational energy only) if there were no influence at work restraining rotation, such as is postulated by the theory of quanta.

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[1] Cf. Partington, *P. Z.*, 1914, **15**, 601, 775.

[2] Capstick, *P. T.*, 1894, **185**, 1; 1895, **186**, 567; Strecker, *A. P.*, 1881, **13**, 20; 1882, **17**, 85.

[3] Partington, *F. S.*, 1922, **17**, 734.

[4] G. W. Todd, *P. M.*, 1920, **40**, 357.

In considering the experimental results, it must be remembered that the latter usually require corrections of various kinds.[1]

TRUE SPECIFIC HEATS OF GASES.

Gas.	Temp. °C.	C_p/C_v.	C_p g. cals.	C_v g. cals.
Ammonia [2]	14·5	1·308	8·77	6·70
Sulphur dioxide [2]	13·2	1·290	9·47	7·34
Carbon dioxide [2] [3]	20	1·303	8·76	6·72
Oxygen [4]	20	1·3946	7·06	5·06
Nitrogen [4]	20	1·4045	6·92	4·93
Nitrous oxide [5]	12·2	1·302	8·80	6·76
Nitric oxide [5]	7·6	1·400	6·99	4·99
Chlorine [6]	18	1·353	8·06	5·96

NITROGEN.

$C_v = 4{\cdot}817 + 0{\cdot}00038T + 0{\cdot}0_7 28T^2$ (true).

Temp. °C.	C_v.	C_p.	C_p/C_v.
16·7	4·928	6·923	1·405
100	4·962	6·953	1·402
200	5·003	6·992	1·398
300	5·044	7·032	1·394
400	5·085	7·073	1·391
500	5·127	7·114	1·388
600	5·170	7·157	1·385
700	5·213	7·200	1·381
800	5·258	7·245	1·378
900	5·301	7·288	1·375
1000	5·345	7·332	1·372

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[1] See Partington, *P. R. S.*, 1921, **100** (A), 27; also § 37.

[2] Partington and Cant, *P. M.*, 1922, **43**, 369.

[3] Partington, *P. R. S.*, 1921, **100**, 27.

[4] Partington and Howe, *P. R. S.*, 1924, **105**, 225.

[5] Partington and Shilling, *P. M.*, 1923, **45**, 416.

[6] Partington, *P. Z.*, 1914, **15**, 601, 775.

OXYGEN.

$$C_v = 4\cdot982 + 0\cdot00021T + 0\cdot0_7 55\,T^2 \text{ (true).}$$

Temp. °C.	C_v.	C_p.	C_p/C_v.
16·5	5·049	7·046	1·396
100	5·068	7·060	1·393
200	5·093	7·083	1·391
300	5·120	7·108	1·388
400	5·148	7·136	1·386
500	5·177	7·165	1·384
600	5·207	7·195	1·382
700	5·239	7·227	1·379
800	5·271	7·259	1·377
900	5·303	7·290	1·375
1000	5·338	7·325	1·372

AIR.[1]

$$C_v = 4\cdot850 + 0\cdot00035T + 0\cdot0_7 277T^2 \text{ (true).}$$

Temp. °C.	C_v.	C_p.	C_p/C_v.
15·3	4·953	6·948	1·403
100	4·984	6·975	1·400
200	5·022	7·011	1·396
300	5·060	7·048	1·393
400	5·097	7·084	1·390
500	5·137	7·124	1·387
600	5·177	7·164	1·384
700	5·216	7·203	1·381
800	5·257	7·244	1·378
900	5·300	7·287	1·375
1000	5·343	7·330	1·372

128. Specific Heats of Solids: Dynamical Theory.—By an extension of the theory of gases to solids, Boltzmann[2] obtained a result in harmony with the law of Dulong and Petit[3]: for solid elements the product *specific heat* × *atomic weight* = *atomic heat* = 6·4. A solid element is composed of atoms each *oscillating* about a fixed centre. The total energy is partly kinetic and partly potential. Since the solid has a finite compressibility the atoms are maintained at small distances apart by forces, one set opposing approximation of the atoms, the other set tending to draw the atoms together. In the normal state these forces are in equilibrium.

---

[1] Partington and Shilling, *F. S.*, 1923, **18**, 386.

[2] *W. B.*, 1871, **63**, (2), 731; cf. F. Richarz, *Z. an. C.*, 1908, **58**, 356; **59**, 146; A. Wigand, *A. P.*, 1907, **22**, 64.

[3] See the author's "Inorganic Chemistry," chapter xxiii.

When an atom is drawn out of its equilibrium position through a distance r the force tending to restore it may be assumed proportional to the displacement, *i.e.*, equal to $\mathrm{A}r$. The potential energy of the displaced atom is $\mathrm{A}\int_0^r rdr = \mathrm{A}r^2/2$. If the atom is supposed to execute a circular motion about the position of equilibrium, and if v is the velocity, the centripetal force is $mv^2/r = \mathrm{A}r$. Hence $\frac{1}{2}mv^2 = \mathrm{A}r^2/2$. Thus, *kinetic energy* = *potential energy*.[1]

Suppose the solid in contact with a monatomic gas; when temperature equilibrium is reached, assume the theory of equipartition. The number of degrees of freedom of the atom of solid is 3, ∴ kinetic energy per mol = $3/2 \,.\, \mathrm{RT}$ = potential energy, ∴ total energy = $3\mathrm{RT} = \mathrm{U}$. Thus:

$$\mathrm{C}_v = \partial \mathrm{U}/\partial \mathrm{T} = 3\mathrm{R} = 3 \times 1{\cdot}987 = 5{\cdot}96 \text{ gm. cal} \quad . \quad . \quad (351)$$

fairly close to the value $\mathrm{C}_p = 6{\cdot}4$ (Dulong and Petit's law; cf. § 131).

There is an objection to Boltzmann's theory. At very low temperatures the oscillations would be small, and the proportionality between force and displacement should then be very exact. But the atomic heats, instead of approaching the value 5·96 at very low temperatures, become very much smaller and probably vanish at the absolute zero. In the case of the diamond the atomic heat vanishes at 30° K. Boltzmann's theory has been replaced by the Quantum Theory.

129. The Quantum Theory.—In his investigations on the exchange of energy between radiation and matter, Planck, in 1900,[2] concluded that the energy of a linear resonator, consisting of a mobile electric charge which may be set in vibration by the electric fields of waves impinging on it, increases *per saltum* in whole multiples of a quantity $\epsilon = h\nu$, where h is a universal constant, and ν the frequency. The amount of energy, $h\nu$ is called the *quantum* corresponding with the frequency ν.

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[1] Nernst, *Z. E.*, 1911, **17**, 266.

[2] Cf. "Theorie der Wärmestrahlung," 4th edit., 1921.

For the present purpose, the *quantum hypothesis* may be stated in the following form: *a resonator is capable of taking up or losing energy only in whole multiples of the quantum,* ϵ.

The value of h, or *Planck's constant*, in absolute units (*erg* × *second*), is $6{\cdot}55 \times 10^{-27}$ (see § 133).

130. Specific Heat of a Monatomic Solid.—The application of the quantum hypothesis to solids was first made by Einstein.[1] The following treatment is due to D. L. Chapman; [2] the others are too difficult to give here.

If resonators of period ν are attached to gas molecules, the quantum theory shows that there will be vibrators possessing energies 0, $h\nu$, $2h\nu$, etc., but none with intermediate amounts of energy. Let N_0 = number of atoms with zero energy, N_E = number of atoms with energy E. Suppose the exchange of quanta takes place between the resonators (oscillators) according to the equation:

$$A_0 + nh\nu \rightleftarrows A_E$$

where A_0 is an atom with zero energy, A_E one with energy $E = nh\nu$. Equation [247] then gives:

$$d \ln (N_E/N_0)/dT = Q/RT^2 = nh\nu/kT^2$$

$$\therefore \quad \ln (N_E/N_0) = -nh\nu/kT + \text{const.}$$

$$\therefore \quad N_E = CN_0 e^{-nx} \text{ where } x = h\nu/kT$$

The value of the constant C is assumed by Chapman to be unity, but a particular value is not required.

The *mean energy* of a linear oscillator will be ($e^{-0} = 1$):

$$\frac{h\nu \,.\, e^{-x} + 2h\nu \,.\, e^{-2x} + 3h\nu \,.\, e^{-3x} + \ldots}{1 + e^{-x} + e^{-2x} + e^{-3x} + \ldots} = h\nu/(e^x - 1) \quad . \quad (352)$$

which is Planck's formula.

A material atom may be replaced by *three* linear oscillators ∴ per mol:

$$\mathbf{U = 3N_0 h\nu/(e^x - 1) \quad . \quad . \quad . \quad . \quad (353)}$$

which is Einstein's formula.

Nernst puts $h/k = \beta = 4{\cdot}77 \times 10^{-11}$; $h = R\beta/N_0$,

$$\therefore \quad U = 3R\beta\nu/(e^{\beta\nu/T} - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (354)$$

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[1] *A. P.*, 1907, **22**, 180, 800; 1911, **34**, 170; cf. Hasenöhrl, *P. Z.*, 1911, **12**, 931; P. Frank, *ibid.*, 1912, **13**, 506; F. A. Lindemann, *Dissertation*, Berlin, 1911; Bichowsky, *P. R.*, 1918, **11**, 58; Nernst, *Z. E.*, 1911, **17**, 270; "Lehrbuch," 8-10 Aufl., 1921, p. 268.

[2] *Ann. Rep. C. S.*, 1914, **2**.

The contribution in kinetic energy per degree of freedom = $(R/2)\beta\nu/(e^{\beta\nu/T} - 1)$, whilst on the theory of equipartition it is $(R/2) . T$, always greater.

When $\beta\nu/T$ is very small, $e^{\beta\nu/T} = 1 + \beta\nu/T \quad \therefore \quad (R/2) . \beta\nu/(e^{\beta\nu/T} - 1) = (R/2) . T$, approximately, in agreement with Dulong and Petit's law.

By differentiation of (354) with respect to T:

$$C_v = \partial U/\partial T = 3R \left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} . \quad . \quad . \quad (355)$$

When $\beta\nu/T$ is very small this reduces to 3R (Dulong and Petit's law).

When $\beta\nu/T$ is very large, (355) may be written:

$$C_v = 3R\ (\beta\nu/T)^2 e^{\beta\nu/T}/(e^{\beta\nu/T})^2 = 3R(\beta\nu)^2/T^2 e^{\beta\nu/T}.$$

Now (*H. M.* § 35):

$$T^2 e^{\beta\nu/T} = T^2 + T\beta\nu + (\beta\nu)^2/2\,! + (\beta\nu)^3/T . 3\,! + \ldots$$

the limiting value of which, when $T = 0$, is infinity

$$\therefore \qquad \text{Lim } C_v = 0 \text{ when } T = 0 \quad . \quad . \quad . \quad . \quad . \quad (356)$$

This was considered in § 124, and is found by experiment (§ 4).

Krasê[1] gives $C_v = 2{\cdot}91 + 2{\cdot}89 \tanh 2{\cdot}95 \log \frac{T}{\theta}$, where θ is a constant. Linhart[2] gives $C_v = 5{\cdot}966\ kT^K/(kT^K + 1)$, where k, K are constants. For Cu: $\log k = -5{\cdot}4955$, $K = 2{\cdot}900$. Pólányi[3] shows that $C_v \longrightarrow 0$ as $p \longrightarrow \infty$ if T is finite.

131. Comparison with Experiment.—Equation (50a) gives the difference between C_p and C_v[4] in terms of the compressibility, but as the values of a and η for low temperatures are not known in most cases, an empirical equation[5]:

$$C_v = C_p - 0{\cdot}0214\ C_p^2\ T/T_m \quad . \quad . \quad . \quad . \quad (357)$$

where T_m is the melting-point (absolute), is used. In most cases the following formula (A = const.) is sufficient[6]:

$$C_v = C_p - AT^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (358)$$

---

[1] *J. A. C. S.*, 1922, **44**, 784.

[2] *Ibid.*, 141.

[3] *Z. p. C.*, 1913, **83**, 339.

[4] G. N. Lewis, *J. A. C. S.*, 1907, **29**, 1165, concludes that, within the limits of experimental error, C_v × at. wt. is the same at 20° for all solid elements with at. wts. greater than 40. In the case of extremely electro-positive metals C_v is abnormally large; cf. Lewis, Eastman, Rodebush, *N. A.*, 1918, **4**, 25.

[5] Nernst and Lindemann, *Z. E.*, 1911, **17**, 817; Nernst, "Theoret. Chem.," 8–10 Aufl., 276.

[6] Lindemann and Magnus, *Z. E.*, 1910, **16**, 269. For ice the term AT^6 was used.

The following table illustrates the agreement with Einstein's formula (355): it gives too rapid a fall of C_v with temperature:

Copper. $\beta\nu = 240$.

T.	C_v obs.	C_v calc.
88	3·38	3·31
33·4	0·538	0·234
22·5	0·223	0·023

C. L. Lindemann[1] finds that the mean coefficient of thermal expansion of metals at low temperatures is in a constant ratio to the atomic heat: this indicates that $(\partial v/\partial T)_p$ tends to zero at $T = 0$.[2]

132. Nernst-Lindemann Formula.—Nernst and F. A. Lindemann proposed[3] the empirical equation:

$$C_v = \frac{3}{2}R\left[\left(\frac{\beta\nu}{T}\right)^2 \frac{e^{\beta\nu/T}}{(e^{\beta\nu/T}-1)^2} + \left(\frac{\beta\nu}{2T}\right)^2 \frac{e^{\beta\nu/2T}}{(e^{\beta\nu/2T}-1)^2}\right] \quad (359)$$

which agrees well with the experimental values:

KCl. $\beta\nu = 218$.[4]

T.	C_v obs.	C_v calc. Einstein.	C_v calc. N.L.
331	6·16	5·90	6·06
86	4·36	3·54	4·43
52·8	2·80	1·70	2·97
30·1	0·98	0·235	1·23
22·8	0·58	0·039	0·61

The most satisfactory equation, however, is that of Debye,[5] which is considered in § 136.[6] In this the idea of more than one frequency (two are used in 359) is considerably extended, but on a theoretical (not empirical) basis.

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[1] *P. Z.*, 1911, **12**, 1197; Grüneisen, *A. P.*, 1908, **26**, 211; 1910, **33**, 65.

[2] Cf. Valentiner and Wallot, *A. P.*, 1915, **46**, 837.

[3] *B. B.*, 1911, p. 494.

[4] Determined by the residual ray method by Rubens and Hollnagel, *P. M.*, 1910, **19**, 761; see § 135 (2).

[5] Comparison of equations: Ewald, *A. P.*, 1914, **44**, 1213; Jüptner, *Z. E.*, 1913, **19**, 711; 1914, **20**, 10, 105, 187.

[6] An approximate law, corresponding with that of Dulong and Petit for elements, states that the molecular heat of a solid compound is equal to the sum of the atomic heats of its constituents (see the tables in Berthelot's "Thermochimie," I., 122 ff.). This is nearly true, even when the atomic heats are abnormal.

133. **Planck's Constant.**—The constant h appears in a large number of different regions of physical research.

1. *Radiation.*—The first application of the quantum theory was in the study of radiation. It is known by experiment that the intensity and character of radiation issuing from a very small aperture in a vacuous enclosure, maintained at a given temperature, depend only on the temperature, are independent of the material of the enclosure, and are identical with those of radiation from a perfectly black body at the same temperature.[1]

The radiant energy per c.c. in a space traversed by radiation is defined as the *radiation density*, ρ.

According to Planck,[2] the density of radiation in equilibrium with a Hertzian oscillator, consisting of an electron vibrating about a fixed positive charge in simple harmonic motion is, for a fixed frequency ν :

$$\rho_\nu = 8\pi\nu^2 \mathrm{E}_\nu / c^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (360)$$

where c = velocity of light, E_ν = energy of the oscillator.

On the *equipartition theory* ($f = 1$, § 127), $\mathrm{E}_\nu = k\mathrm{T} = \mathrm{RT}/\mathrm{N}_0$

$$\therefore \quad \rho_\nu = 8\pi k \nu^2 \mathrm{T}/c^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (361)$$

which is *Rayleigh's radiation formula.*[3]

On the *quantum theory*, $\mathrm{E}_\nu = h\nu/(e^{h\nu/k\mathrm{T}} - 1)$

$$\therefore \quad \rho_\nu = \frac{8\pi h \nu^3}{c^3} / (e^{h\nu/k\mathrm{T}} - 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (362)$$

which is *Planck's radiation formula.*[4]

Rayleigh's formula is in agreement with experiment for the conditions assumed, viz., for long waves, *i.e.*, small values of ν. It is a special case of Planck's formula, which holds over a large range of wave-lengths.

From radiation measurements the values :

$$k = 1{\cdot}369 \times 10^{-16}\ \mathrm{erg}/1^\circ\,; \quad h = 6{\cdot}525 \times 10^{-27}\ \mathrm{erg.\ sec.}$$

have been found. Planck's formula has been confirmed by experiments of Rubens and Kurlbaum, Paschen, and Warburg.[5]

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[1] Preston, "Theory of Heat"; Henning, "Temperaturmessung," 1915, pp. 128 ff.; Campbell, "Modern Electrical Theory," 1913, 222 ff.

[2] "Theorie der Wärmestrahlung," 1906, p. 124.

[3] *P. M.*, 1900, **49**, 539 (given for very long waves only, and not as a general formula); Swan, *P. R.*, 1916, **7**, 154.

[4] *A. P.*, 1901, **4**, 553. Radiation formulæ for the solid state deduced without the help of quanta: cf. Byk, *A. P.*, 1913, **42**, 1417; Callendar, *P. M.*, 1913, **26**, 787; 1914, **27**, 870; Brillouin, *A. de P.*, 1914, **1** [ix.], 13, 163, 433; Tolman, *P. R.*, 1914, **3**, 244; and Ratnowsky, *D. p. G.*, 1915, **17**, 64.

[5] It has been criticised by Nernst and Wulf, *D. p. G.*, 1919, **21**, 294.

2. *Photoelectric Effect.*—The emission of electrons by a metal when exposed to light is known as the *photoelectric effect.* For each metal there is a limiting frequency, ν_0, of the light, below which no electrons are emitted. An electron of mass m emitted with velocity v has the energy $mv^2/2$. If the metal is given a positive charge, and is at the potential V, the electron is attracted back to the plate, and if V has such a value that the electrons *all* fall back on the plate, $eV = mv^2/2 =$ *maximum* energy of the photo-electron. If ν is the frequency of the (mono-chromatic) light used, and if one quantum liberates one photo-electron : $eV = mv^2/2 = h\nu - P$, where P is the energy used up by the electron in finding its way out of the metal. By plotting the voltage applied to stop all electrons from sodium and lithium exposed to monochromatic radiation (mercury lines) against the frequency (ν) of the radiation, Millikan[1] obtained a straight line, from the slope of which h was found to be $6{\cdot}57 \times 10^{-27}$ erg. sec. for Na, and $6{\cdot}58 \times 10^{-27}$ for Li. This is probably the most exact determination of h.

3. *Law of Photochemical Equivalence.*—A theory of photochemical action proposed by Einstein[2] assumes that each molecule decomposed requires the absorption of one quantum, $h\nu$, so that if the energy U is absorbed per mol, $U = N_0 h\nu$. The application of this theory is rendered difficult by secondary effects, but according to Noddack[3] the equation is verified in the reactions between bromine and *cyclo*hexane ([illegible]) and chlorine and trichlorobromomethane (liquid). A solution of chlorine in the latter on exposure to light probably undergoes the following reactions :

$$
\begin{aligned}
Cl_2 + CBrCl_3 + h\nu &= CCl_4 + Cl + Br\,; \\
Cl + CBrCl_3 + Br &= CCl_4 + Br_2.
\end{aligned}
$$

The bromine could be determined spectrophotometrically ; the radiation absorbed was determined by a thermopile as usual. The quantum $h\nu$ is absorbed by the chlorine molecule, which is activated. This active state has a given "life" (calculated as 10^{-10} sec.), during which it may react with an acceptor. If no acceptor is present, the activated molecule gives up energy in the form of other quanta (luminescence, or heat), or transfers it to indifferent molecules, causing a general rise of temperature.

In many other cases investigated the amount of chemical decomposition is very much greater than it should be on the law of Photochemical Equivalence.[1]

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[1] *P. R.*, 1916, **7**, 355.

[2] *A. P.*, 1912, **37**, 832.

[3] *Z. E.*, 1921, **27**, 359 ; cf. Baly and Barker, *C. S.*, 1921, **119**, 653.

4. *Optical Spectra.*—Modern researches in radioactivity have led to the view (Rutherford) that the atom consists of a positive nucleus, concentrated into a very small volume as compared with the volume of the atom, surrounded by electrons. According to Bohr [2] these electrons describe orbits about the nucleus. In the simplest atom, that of hydrogen, there is one electron describing a circular orbit around the nucleus. Let e, m be the charge and mass of the electron, $E = ze$ the charge on the nucleus. If a is the radius of the circular orbit of the electron, v its velocity, and ω its angular velocity ($= 2\pi$. rotation frequency), the equation of centrifugal force gives : $eE/a^2 = ma\omega^2$, or $ma^3\omega^2 = eE = e^2z$.

According to Bohr the moment of momentum of the rotating electron is a whole multiple of $h/2\pi$ (quantum hypothesis), where h is Planck's constant, hence :

$$ma^2\omega = nh/2\pi \quad (n = 1, 2, 3, \text{etc.})$$

Only those orbits which fulfil this condition are possible, hence the radii of the possible quantum orbits are :

$$a_n = n^2h^2/4\pi^2e^2zm \quad (n = 1, 2, 3, \text{etc.})$$

and the corresponding frequencies of rotation are :

$$\omega_n = 8\pi^3e^4z^2m/n^3h^3.$$

The energy (kinetic + potential) is :

$$\mathrm{U} = \tfrac{1}{2}mv^2 + (-eE/a) = \tfrac{1}{2}ma^2\omega^2 - e^2z/a = -e^2z/2a.$$

By substituting for a, we find the permissible energies :

$$\mathrm{U}_n = -2\pi^2e^4z^2m/h^2n^2.$$

According to the hypothesis of Bohr, which is in contradiction to the classical electromagnetic theory of light, the atom will radiate energy only when the electron springs from one permissible quantum orbit to another ; no energy is radiated when the electron is revolving in a circular quantum orbit. If U_m and U_n are the energies in the mth and nth orbits, the frequency, ν, of the monochromatic radiation emitted (which is not the same as ω, the frequency of rotation of the electron) will be given by the quantum relation : $\mathrm{U}_m - \mathrm{U} = h\nu$, hence :

$$\nu = \frac{2\pi^2e^4mz^2}{h^3}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = Nz^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

where $N = 2\pi^2e^4m/h^3$.

---

[1] Cf. Lind, "Chemical Effects of α-Particles and Electrons," New York, 1921.

[2] *P. M.*, 1913, **26**, 1, 476, 857.

The above expression, when $z = 1$, is precisely that discovered empirically by Balmer for the frequencies in the series spectrum of hydrogen, provided that $n = 2$, and m has the values 3, 4, 5, etc. The constant N which appears in the empirical formula is known as Rydberg's constant, and has been determined experimentally from spectrum measurements as $3{\cdot}29 \times 10^{15}$. Bohr's theory enables us to calculate the value of this from the values of e, m and h, as $3{\cdot}294 \times 10^{15}$. Not only is the Balmer series given by Bohr's formula, but for the values $n = 1$, $m = 2, 3, 4$, etc., we get the Lyman ultraviolet spectrum of hydrogen, and for $n = 3$, $m = 4, 5, 6$, etc., the infra-red Bergmann series, the first two lines of which were measured by Paschen.

In the case of helium, $z = 2$, and the atom consists of two electrons moving about the doubly charged nucleus. The ion formed by the loss of one electron consists of the doubly charged nucleus with one electron revolving around it, and the above formula will therefore apply with $z = 2$. The series emitted will be given by :

$$\nu = 4N\ (1/n^2 - 1/m^2)$$

and if $n = 3$, $m = 4, 5, 6$, etc., we get the so-called " principal series of hydrogen " observed by Fowler with a mixture of hydrogen and helium. With $n = 4$, $m = 5, 6, 7$, etc., we get the so-called " second subsidiary series of hydrogen " observed by Pickering. Both series had previously been incorrectly ascribed to hydrogen.

The calculation of the spectra series of hydrogen and helium by Bohr is one of the conspicuous triumphs of the quantum theory.[1]

5. *X-Ray Spectra.*—With a given anti-cathode material, bombarded by the electrons proceeding from the cathode in the X-ray tube, it is found that two kinds of X-radiation are produced : *impact radiation,* consisting of a continuous spectrum of wave-lengths, and *characteristic radiation,* depending on the material of the anti-cathode, and characteristic for each element. Moseley [2] found that the characteristic spectrum lines could be arranged in series, as in optical spectra, the wave-lengths of corresponding lines being very simply related to the *atomic number,* z, of the element: $\nu = A\ (z - b)^2$, where A and b are constants, the same for all elements.

Three series of lines have been discovered (with traces of a fourth): the short wave K series, the longer wave L series, and a still longer wave M series. Moseley found[1] that the K_α (first line of K series) frequency of an element could be represented, approximately, by a formula of the same type as that deduced by Bohr for the optical spectrum:

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[1] Cf. Bohr, *Z. P.*, 1922, **9**, 1; Fowler, "Report on Spectra," Phys. Soc., 1922.

[2] *P. M.*, 1913, **26**, 1024; 1914, **27**, 703.

$$\nu_{K_\alpha} = N(z - 1)^2 (1/1^2 - 1/2^2).$$

Consider next the *continuous* X-ray spectrum (impact radiation). If $\lambda_{min.}$ is the series limit, or the line of smallest wave-length, emitted, this will be related to the tube voltage by the formula:

$$eV = h\nu_{max.} = hc/\lambda_{min.}$$

The rest of the spectrum can be emitted with this voltage, since each value of ν is *less* than $\nu_{max.}$ This result is independent of the material of the anti-cathode, and in this way Duane and Hunt[2] found $h = 6{\cdot}51 \times 10^{-27}$ erg. sec. Newer researches[3] give values from $6{\cdot}53 \times 10^{-27}$ to $6{\cdot}58 \times 10^{-27}$, in excellent agreement with other values.

6. *Ionisation and Resonance Potentials.*[4]—When metallic atoms in the state of vapour are bombarded by electrons, the collision is elastic (*i.e.*, the electron rebounds with unchanged energy), unless the energy of the colliding electron exceeds a certain limiting value, U_r. When this is reached the electron loses the whole of its energy to the atom, and radiation is emitted in the form of a single line spectrum. Thus, mercury emits the single line 2537 Å. (Wave-lengths are usually measured in Ångstrom units; 1 Å $= 10^{-10}$ metre. If V is in volts, and λ is the wave-length in Å, the equation $eV = h\nu = hc/\lambda$, where c is the velocity of light, which is used below, becomes $V = 12331/\lambda$.) This result is easily explained on Bohr's theory if it is assumed that there is a single electron orbit outside the rest of the atom. If this is called orbit 1, then the work required to cause the electron to spring to orbit 2, with more energy, will be $U_2 - U_1 = h\nu_{2,1}$. In falling back from orbit 2 to orbit 1 the electron then emits the line of frequency $\nu_{2,1}$. Hence, on the quantum theory: $U_r = h\nu_{2,1}$. This has been verified by experiment. In the case of sodium vapour, emission occurs first when the accelerating voltage of the electron is $V_r =$

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[1] Cf. Sommerfeld, "Atombau und Spektrallinien," 1922, Eng. Tr., 1923.

[2] *P. R.*, 1916, **6**, 166.

[3] Webster, *ibid.*, 1916, **7**, 599; Webster and Clarke, *N. A.*, 1917, **3**, 181; Blake and Duane, *P. R.*, 1917, **9**, 568; **10**, 93, 624; Wagner, *P. Z.*, 1920, **21**, 621; Duane, *P. R.*, 1916, **7**, 143; Webster, *P. R.*, 1920, **16**, 31.

[4] See Bulletin of the National Research Council, Vol. **2**, Pt. **2**, No. 10 (Washington, 1921).

2·2 volts, the so-called *resonance potential.* In the case of mercury vapour, the value of the resonance potential is calculated as $V_r = 12331/\lambda_{2,1} = 4{\cdot}86$ volts. The observed value is 4·9 volts.

When more and more energy is given to the colliding electron, the outer electron of the atom will be carried to higher and higher quantum orbits. At a certain critical energy the electron will be removed altogether from the atom, *i.e.*, removed to infinity, and the atom is *ionised.* In falling back to the atomic orbits the electron will give up energy and a spectrum of many lines will be emitted, each corresponding with a quantum orbit. This is the *ionisation spectrum,* and the voltage required to produce it is the *ionisation potential,* V_∞. The ionisation energy is equal to the quantum corresponding with the last line of the spectrum, *i.e.*, the series limit. In the case of sodium, V_∞ was found to be 5·13 volts, hence $U_\infty = eV_\infty/300 = 8{\cdot}17 \times 10^{-12}$ erg. The limit of the principal series in the ionisation spectrum has the wave-length $\lambda_{\infty, 1} = 2413$ Å, hence $h\nu_{\infty, 1} = 8{\cdot}14 \times 10^{-12}$, in agreement with U_∞.

The best values of *h*, calculated by seven different methods, are as follows:[1]

Method.	*h* in erg sec. × 10^{27}.
Stefan-Boltzmann total radiation constant	6·551 ± 0·009
Wien constant	6·557 ± 0·013
Rydberg constant (Bohr's theory) . .	6·542 ± 0·011
Einstein photoelectric equation. . .	6·578 ± 0·026
Quantum relation applied to X-radiation .	6·555 ± 0·009
Lewis and Adams' theory of ultimate rational units	6·560 ± 0·014
Quantum relation applied to ionisation and resonance potential	6·5543 ± 0·0025

The most probable value (assuming Millikan's value for the electronic charge, $4{\cdot}774 \times 10^{-10}$ E.S.U.) is

$$h = (6{\cdot}5543 \pm 0{\cdot}0025) \times 10^{-27} \text{ erg sec.}$$

According to Sanford[2] *h* is not a constant; it may be replaced in the equation $\frac{1}{2}mv^2 = h\nu$ by the expression $4{\cdot}25 \log m + 2{\cdot}5$, which is a function of *m*, the transverse mass of the electron, with great improvement in the accuracy of this equation.

134. The Second Quantum Theory.

—In a modified form of the quantum theory proposed by Planck[3] it is assumed that the *absorption* of radiation is continuous, but that *emission* takes place discontinuously when the oscillator has absorbed a whole number of quanta. This gives the result that the mean energy of an oscillator when T = 0 is not zero but equal to $h\nu/2$. This makes no difference to the formulæ for the specific heats, as the constant term $h\nu/2$ in the energy (" Nullpunktsenergie ") vanishes on differentiation, but it affects the results where the energy itself is concerned.

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[1] Birge, *P. R.*, 1919, **14**, 361.

[2] *P. R.*, 1920, **16**, 338.

[3] "Wärmestrahlung," 4th edit., § 168.

135. Determination of the Atomic Frequency.—The association of quanta $h\nu$ with atoms implies the existence of a characteristic frequency ν of the latter, which may be called the *atomic frequency.* Several methods for the determination of ν have been used.

1. *From Specific Heats.*—The value of ν which gives the best results in the atomic heat equations (355) or (359) may be taken as the atomic frequency.

2. *Method of Residual Rays.*[1]—According to modern views of crystal structure [2] the charged ions of a salt, such as NaCl, are assumed to be present as separate units in the crystal lattice. These ions can oscillate in alternating electric fields, such as are supposed on Maxwell's theory to exist in light or radiant heat. For a certain frequency of oscillation in the incident radiation we should expect to obtain resonance and strong reflection. Such radiations are known as *residual rays* (" Reststrahlen "), since they remain after successive reflections of infra-red radiation from a number of pieces of solid. This method has been used chiefly by Rubens [3] and his co-workers. The table in § 132 shows that the values of ν obtained in this way are in good agreement with those found from the specific heats.

3. *Elastic Properties.*—The formula :

$$\nu = 2{\cdot}8 \times 10^7 A^{-\frac{1}{3}} \eta^{-\frac{1}{2}} \rho^{-\frac{1}{6}} \quad . \quad . \quad . \quad . \quad . \quad (363)$$

where A = at. wt., η = compressibility, ρ = density, was deduced by Einstein.[4] According to Lindemann [5] the numerical constant is 3·58 instead of 2·8. The values thus found agree with those from the specific heats.

4. *Melting Point.*—An ingenious method for the determination of ν is due to F. A. Lindemann (1910).[6] At the melting point of a solid he assumes that the amplitudes of the atomic or molecular oscillations become so large that the particles collide with one another, and the energy is shared (cf. below).

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[1] See papers by Rubens and collaborators in *A. P.* and *B. B.* since 1910.

[2] Cf. Bragg, " X-Rays and Crystal Structure."

[3] Cf. Jellinek, " Gasreaktionen," pp. 412 ff. ; 575 ff.

[4] *A. P.*, 1911, **34**, 170. Similar formulæ were given by Madelung, *P. Z.*, 1910, **11**, 898, and by Sutherland, *P. M.*, 1910, **20**, 657.

[5] Nernst, " Lehrb.," 281, where other methods of finding ν are given.

[6] *P. Z.*, 1910, **11**, 609 ; Pagliani, *N. C.*, 1918, **15**, 103.

If ν is the frequency of the atom (a complete period),

$$v = 2\pi r_0 \nu,$$

where v = velocity, and r_0 = radius of circle of oscillation at the melting point. The mean energy of the atom (kinetic + potential) is (§ 128): $mv^2 = 4m\pi^2 r_0^2 \nu^2$. This is also given by (354): $3k\beta\nu/(e^{\beta\nu/\mathrm{T}} - 1) = 3k\mathrm{T}_0$, approximately, since $\beta\nu/\mathrm{T}$ is small at the melting point, T_0. Hence:

$$4m\pi^2 r_0^2 \nu^2 = 3k\mathrm{T}_0$$

or

$$\nu = \text{const.} \times \sqrt{\mathrm{T}_0/mr_0^2}.$$

In a solid body we can put V = atomic volume, proportional to r_0^3, and the constant is then determined experimentally with one element, *e.g.*, Ag. Thus:

$$\nu = 2{\cdot}80 \times 10^{12}\sqrt{\mathrm{T}_0/AV^{\frac{2}{3}}} \quad . \quad . \quad . \quad . \quad (364)$$

where A = at. wt.

Honda[1] takes the constant $3{\cdot}08 \times 10^{12}$. He assumes linear oscillations in the solid and allocates to each atom the energy $h\nu/(e^{h\nu/k\mathrm{T}} - 1)$, or $\mathrm{R}\beta/(e^{\beta\nu/\mathrm{T}} - 1)$ per mol. The results agree with those from atomic heats. Rotational energy in the solid is assumed to be small, except at very high temperatures. The molecules set free on liquefaction are assumed to retain the energy referred to, but to acquire also rotational energy corresponding with 2 or 3 degrees of freedom, the energy per degree of freedom being $\frac{1}{2}h\nu$. The total energy acquired on fusion will then be, per gram-molecule, $\mathrm{N}_0 h\nu = \mathrm{U}$ or $\frac{3}{2}\mathrm{U}$, according as the liquid molecules have an axis of symmetry or not. Thus $\mathrm{ML}_f = \frac{1}{2}n\mathrm{U}$, where $n = 2$ or 3. The value of U is calculated by the formula given above with a value of ν, the frequency, given by Lindemann's equation, and it is noteworthy that although n is 2 in the case of many elements, the value 3 is also required for some elements (*e.g.*, zinc) usually assumed to be monatomic. Honda obtains a fairly satisfactory agreement for a number of elements and compounds, although in some of the latter values of n much higher than 3 have to be assumed (*e.g.*, 6 for KF, 7 for $\mathrm{PbCl_2}$).

It is to be expected on theoretical grounds that the energy content of molecules at the fairly high temperatures of fusion would be more satisfactorily given by the formula of Debye (§ 136).

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[1] *P. R.*, 1918, **12**, 425; *P. M.*, 1923, **45**, 189; cf. Lindemann, *P. M.*, 1923, **45**, 1119.

The following table gives some results[1] of the calculation :

Substance.	M.	ML_f obs.	T.	$\nu \times 10^{-12}$.	$\beta\nu$.	$\frac{U_f}{2T}$.	$\frac{ML_f}{T}$.	n.
Hydrogen	2	16	14	2·669	129·8	0·0247	1·14	4·6
Nitrogen	28	192	62·5	1·402	68·17	0·645	3·07	4·8
Chlorine	70	814	169·5	1·578	76·72	0·835	4·790	5·7
Mercury	200	550	234·3	1·361	61·19	0·89	2·34	2·6
Bromine	159·8	1293	265·7	1·069	51·95	0·99	4·879	5
Iodine	254	1487	386·5	1·023	49·75	0·944	3·84	4
Potassium	39	574	336·5	2·53	123	0·875	1·71	1·9
Sodium	23	632·5	371	2·921	142·1	0·86	1·68	1·9
Lead	207	1118	600	1·99	96·8	0·934	1·86	2·0
Sodium hydroxide	40	1610	633	4·601	223·8	0·868	2·543	2·9
Potassium fluoride	58	6275	1133	4·737	230·3	0·92	5·525	6·0
Silver bromide	187	2370	703	1·92	93·4	0·945	1·89	2·0
Lead chloride	178	5150	764	1·40	65·1	0·955	6·67	7·0
Barium chloride	208·3	5581	1232	1·900	92·39	0·96	4·471	4·7
Acetic acid	60·03	2641	289·7	1·757	85·43	0·888	10·91	12·3
Phenol	94	2735	313	1·261	61·31	0·923	7·49	8·1
Benzene	78	2340	278·5	1·306	63·5	0·909	8·5	9·4
Benzophenone	182	3950	321	0·7447	36·20	0·9515	12·28	12·9
Naphthalene	128·1	4483·5	353	1·064	51·71	0·941	12·70	13·5

136. **Debye's Theory of the Solid State.**—In a theory of the solid state due to Debye[2] the atomic structure is disregarded, and the heat content is regarded as the energy of elastic waves, the length of which is large compared with the distances between the atoms. There will then not be a single characteristic frequency ν for the solid, but a whole spectrum of frequencies, cut off sharply at a maximum frequency ν_m, imposed by the atomic dimensions.

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[1] Stratton and Partington, *P. M.*, 1922, **43**, 436 ; cf. Allen, *P. Phys. Soc.*, 1916, **29**, 204 ; 1915, **3**, 215 ; Narbutt, *P. Z.*, 1921, **22**, 52 ; Ratnowski, *D. p. G.*, 1914, **16**, 1033.

Latent heats of evaporation : Duclaux, *C. R.*, 1913, **156**, 142 ; Rideal, *P. M.*, 1921, **42**, 156. Pagliani (*A. L.*, 1915, **24**, i., 835 ; *N. C.*, 1916, **11**, i., 118) finds that the metals may be divided into three classes according as the ratio of the entropy (§ 124) to the frequency given by (364) has the mean value 0·36 (alkali metals), 0·146 (groups II., III., IV., VI. and the first series of VIII.), and 0·10 (group V. and the second series of VIII.). The non-metals have the value 0·22 (the constant of equation 364 is taken as $2 \cdot 12 \times 10^{12}$). Sulphur must be assumed to be S_2. Relations with elastic properties are considered.

[2] *A. P.*, 1912, **39**, 789 ; Nernst and Lindemann, *B. B.*, 1912, 1160 ; Born and Kármán, *P. Z.*, 1913, **14**, 65 ; Schrödinger, *P. Z.*, 1919, **20**, 420, 450, 474, 497, 523.

The number of vibrations between the frequencies ν and $\nu + d\nu$ per unit volume is assumed to be:

$$dz = A\nu^2 d\nu$$

where A is a constant.[1]

According to the classical theory the energy associated with each vibration is RT/N_0

$$\therefore \quad U = 3RT = \frac{RTA}{N_0}\int_0^{\nu_m} \nu^2 d\nu = RTA\nu_m{}^3/3N_0$$

$$\therefore \quad A = 9N_0/\nu_m{}^3.$$

On the quantum theory, each vibration is associated with the energy $R\beta\nu/(e^{\beta\nu/T} - 1)N_0$

$\therefore$ this expression must replace RT/N_0 above

$$\therefore \quad U = \frac{RA}{N_0}\int_0^{\nu_m} \nu^2 \,.\, \frac{\beta\nu}{e^{\beta\nu/T} - 1} \,.\, d\nu = \frac{9R}{\nu_m{}^3}\int_0^{\nu_m} \frac{\beta\nu^3}{e^{\beta\nu/T} - 1}\, d\nu.$$

Put $\qquad \beta\nu/T = x \therefore \nu = xT/\beta \therefore d\nu = Tdx/\beta$

$$\therefore \qquad U = 9RT\left(\frac{T}{\beta\nu}\right)^3 \int_0^{\beta\nu/T} \frac{x^3 dx}{e^x - 1} \quad . \quad . \quad . \quad . \quad (365)$$

from which values of U and $C_v = dU/dT$ may be found.[2]

At very low temperatures:

$$U = aT^4, \text{ and } C_v = 3R \,.\, \frac{4\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 = a'T^3 \quad . \quad . \quad (366)$$

where a and a' are constants.

Debye's formula is, in general, very closely verified by experiment:[3]

Copper. $\beta\nu = 323{\cdot}5$.			Lead. $\beta\nu = 88$.		
T.	C_v obs.	C_v calc.	T.	C_v obs.	C_v calc.
15·24	0·0491	0·0486	15·98	1·87	1·87
18·03	0·0792	0·0804	22·4	3·00	3·06
19·58	0·1010	0·1030	30·24	4·06	4·03
21·50	0·1410	0·1365	47·6	5·07	5·04

It is evident from (365) that dU/dT must have the form $3Rf(h\nu_m/kT) = 3Rf(\beta\nu_m/T)$, where the function f is the same for all substances. On the theory of equipartition $f(\beta\nu_m/T) = 1$. Put

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[1] Cf. Jeans, "Dynamical Theory of Gases," 2nd edit., p. 386; Planck, "Wärmestrahlung," 4th edit., pp. 203, 215.

[2] Cf. Nernst, "Grundl. Wärmesatzes," 1918, pp. 78 ff., and Appendix.

[3] Onnes and Keesom (*A. A.*, 1915, **18**, 484) find that C_v for Cu decreases rather more rapidly at very low temperatures than according to Debye's formula $C_v = 464{\cdot}1(T/\theta)^3$. Cf. Griffiths, *P. T.*, 1914, **214**, 319.

$h\nu_m/k = \beta\nu_m = \theta$, a characteristic temperature associated with each substance, then :

$$C_v = 5{\cdot}96 f(\theta/T) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (367)$$

The values of $f(\theta/T)$ for different values of $T/\theta = T/\beta\nu_m$ are given below[1] :

T/θ.	$f(\theta/T)$.	T/θ.	$f(\theta/T)$.	T/θ.	$f(\theta/T)$.
∞	1·000	0·8	0·926	0·20	0·369
4	·997	·7	·904	·15	·213
3	·994	·6	·872	·10	·0758
2	·988	·5	·825	·075	·0328
1·5	·978	·4	·745	·050	·00974
1·0	·952	·3	·607	·025	·00122
·9	·941	·25	·503	·000	·000

Values of θ are : Al 396 ; Cu 309 ; Ag 215 ; Pb 95.

The curve in Fig. 43 gives theoretical values of atomic heats

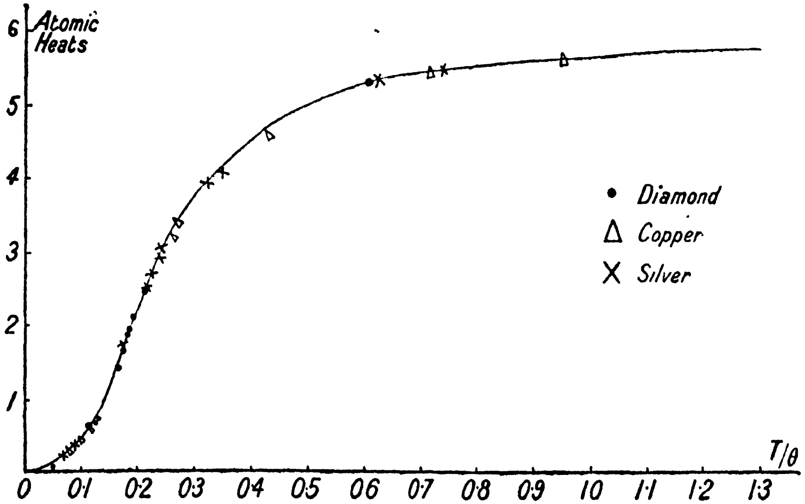

Fig. 43.

found from $f(\theta/T)$; the marks •, Δ, and X give the values found by experiment from the specific heats of diamond, copper, and silver.

The theory of the specific heats of *compounds* is still somewhat indefinite. It appears that C_v may be expressed as a Debye function for the whole molecule, and a sum of Einstein functions (355) for the separate atoms.[2]

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[1] Jeans, " Dynamical Theory of Gases," 2nd edit., p. 424.

[2] Nernst, " Lehrb.," 279 ; " Theory of the Solid State," London, 1914; Schrödinger, *loc. cit.* ; Reiche, "Quantum Theory," 1922, p. 56. R. C. Tolman (*P. R.*, 1914, **4**, 145) gives a formula for the specific heats of solids and liquids at low temperatures which agrees with Debye's, but he deduces it without making

137. Application of the Quantum Theory to Gases.—The energy of a polyatomic gas molecule may, in general, be considered as divided into three parts: (i.) translational kinetic energy of the molecule as a whole; (ii.) rotational energy of the molecule as a whole; (iii.) vibration of the atoms composing the molecule.

It is usually assumed that the translational kinetic energy is always given, even in the most complex molecule, by 3/2 . RT (§ 126).[1] On the theory of equipartition the rotational energy of a diatomic molecule is given by RT (§ 127), and if the vibration is a simple harmonic motion (mean potential energy = mean kinetic energy, § 128), it will be associated with the energy RT. The total energy will then be:

$$E = 3/2 . RT + 2/2 . RT + 2/2 . RT = 7/2 . RT$$

$$\therefore C_v = 7/2 . R = 6{\cdot}93 \text{ gm. cal.}$$

This value is not shown by any diatomic gas. We may assume the vibrational energy taken up in quanta, when:

$$C_v = 3\frac{R}{2} + R\frac{e^x x^2}{(e^x - 1)^2} \quad . \quad . \quad . \quad . \quad . \quad [368]$$

($x = \beta\nu/T$) when there is no rotation, or

$$C_v = 3\frac{R}{2} + 2\frac{R}{2} + R\frac{e^x x^2}{(e^x - 1)^2} \quad . \quad . \quad . \quad . \quad [369]$$

when there is rotation.

Equation [369] was applied by Bjerrum[2] to hydrogen and nitrogen at high temperatures, with fairly satisfactory results. Better results were found when the Nernst-Lindemann function (§ 132) was used in the last term. Hydrogen and nitrogen exhibit no absorption bands in the infra-red, but those found with carbon monoxide and oxygen gave the value of $\nu = c/\lambda$ required by [369].

In the case of triatomic molecules (H_2O, CO_2), Bjerrum[3]

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any assumptions as to the form of the relation connecting energy with temperature and frequency of vibration. For the specific heat of any elastic isotropic body Tolman deduces the following expression:

$$C = 4Av\rho^{\frac{3}{2}}\eta^{\frac{3}{2}}\left\{B\left(\frac{2(1+\sigma)}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \left(\frac{1+\sigma}{3(1-\sigma)}\right)^{\frac{3}{2}}\right\}T^3$$

where σ = Poisson's ratio, A and B are numerical constants, the same for all materials, and v is the volume.

[1] **Cf. Partington, *F. S.*, 1922, 17, 734.**

[2] ***Z. E.*, 1911, 17, 732.**

[3] ***Z. E.*, 1912, 18, 103.**

assumed three frequencies, ν_1, ν_2, ν_3, and (since there are three degrees of freedom of rotation):

$$\therefore \qquad C_v = 3\frac{R}{2} + 3\frac{R}{2} + R\sum_{\nu_1}^{\nu_3}\frac{e^x x^2}{(e^x - 1)^2}$$

or the corresponding formula with the Nernst-Lindemann function in the last term. In the case of CO_2, the frequency of vibration of the two oxygen atoms was taken as $\nu_1 = 0{\cdot}21 \times 10^{14}$; for the frequency of vibration of the two oxygen atoms with respect to the carbon atom, $\nu_2 = \nu_3 = 0{\cdot}48 \times 10^{14}$. The values found from the infra-red absorption spectrum, with wave-lengths $\lambda_1 = 14{\cdot}7\,\mu$ ($\mu = 0{\cdot}001$ mm.), $\lambda_2 = 4{\cdot}3\,\mu$, $\lambda_3 = 2{\cdot}7\,\mu$ ($\nu = \lambda/3 \,.\, 10^{-14}$) also gave satisfactory results. All the frequencies, it is seen, have approximately the same very high value 10^{14}.

The first application of the quantum theory to the *rotational* energy of the molecule was made by Nernst.[1]

Nernst assumed the rotational energies of gas molecules are represented by the Einstein formula, but the rotational frequency $\beta\nu$ is proportional to the square root of the absolute temperature, as on the classical theory: $\beta\nu = a\sqrt{T}$, where a is a constant. The following equation gives the contribution of one degree of freedom to C_v for the rotations:—

$$C_v^{\text{int}} = \frac{R}{4}\cdot\left[\frac{x}{e^x - 1} + e^x\left(\frac{x}{e^x - 1}\right)^2\right]$$

where $x = a/\sqrt{T}$.

The specific heat of hydrogen at constant volume at low temperatures was determined by Eucken,[2] who represented his results for C_v by a constant frequency $\beta\nu$ of 430 in Einstein's equation (f = degrees of freedom = 2):

$$C_v^{\text{int}} = Rx^2\frac{e^x}{(e^x - 1)^2} \text{ where } x = \beta\nu/T.$$

Nernst[3] assumes $\beta\nu = 450$. A constant value of $\beta\nu$ would imply a vibrational, not a rotational, motion. Eucken's calculations show that Einstein's formula with $\beta\nu = 430$ gives too high values at lower temperatures and too low values at higher temperatures. The results are still worse represented by the Nernst-Lindemann formula with $\beta\nu = 570$, which would seem to increase the probability that the energy is vibrational, since Nernst[1] has shown that, in the case of solid bodies, the *molecular* motion is more correctly given by the Nernst-Lindemann (or still more accurately, by the Debye), formula, whilst the *atomic vibrations* are represented by the Einstein formula.

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[1] *Z. E.*, 1911, **17**, 265; also A. Eucken, *B. B.*, 1912, 141; Bjerrum, *N. F.*, 1912, p. 95; O. Sackur, *A. P.*, 1913, **40**, 87; Krüger, *ibid.*, 1916, **50**, 346; **51**, 450; Fokker, *ibid.*, 1914, **43**, 810; van Weyssenhoff, *ibid.*, 1916, **51**, 285; Keesom, *P. Z.*, 1914, **15**, 8; Planck, *D. p. G.*, 1915, **17**, 407, 438.

[2] *B. B.*, 1912, 141.

[3] *D. p. G.*, 1916, **18**, 83.

An attempt to base the theory of rotational energy entirely on the quantum hypothesis was made by Einstein and Stern,[2] but the result is admitted to be unsatisfactory because it replaces the fixed frequency ν in Planck's equation by a mean rotational frequency, dependent on temperature: $U_r = \frac{1}{2}I\bar{\omega}^2 = \frac{1}{2}I(2\pi\bar{\nu})^2$, where I is the moment of inertia, and $U_r = h\bar{\nu}/(e^{h\bar{\nu}/kT} - 1)$.

Ehrenfest[3] considered a molecule rotating about a fixed axis (one degree of freedom), and assumed that the rotational energy would change in multiples of $\frac{1}{2}h\nu$, since the total energy of an oscillator (half kinetic and half potential) changes in multiples of $h\nu$

$$\therefore \quad U_r = \tfrac{1}{2}I(2\pi\nu)^2 = nh\nu/2 \quad (n = 0, 1, 2, 3, \ldots)$$

$$\therefore \quad \nu_n = nh/4\pi^2 I \quad (n = 0, 1, 2, 3, \ldots)$$

and

$$U_r^{(n)} = n^2h^2/8\pi^2 I.$$

Thus, the molecule can rotate only with definite discrete speeds, ν_n, and hence possess definite rotational energies belonging to a series of values of n. The *mean energy* of N_0 molecules is then calculated by an extension of a method used in the kinetic theory of gases. If the probability that a molecule has a rotational energy $U_r^{(n)}$ at a temperature T is w_n, then the mean rotational energy is:

$$\overline{U}_r = \sum_{n=0}^{n=\infty} U_r^{(n)} \,.\, w_n.$$

The value of w_n, on the assumption that all the quantum states have the same *à priori* probability is[4]:

$$w_n = e^{-U^{(n)}/kT} \Big/ \sum_{n=0}^{n=\infty} e^{-U^{(n)}/kT}$$

$$\therefore \quad \overline{U}_r = \frac{h^2}{8\pi^2 I} \cdot \frac{\sum_0^\infty n^2 e^{-n^2 a}}{\sum_0^\infty e^{-n^2 a}}$$

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[1] "Theory of the Solid State," 1913; cf. Born, "Dynamik der Kristallgitter," p. 51; Reiche, "Quantum Theory," 1923, pp. 52 ff.; Latimer, *J. A. C. S.*, 1922, **44**, 94.

[2] *A. P.*, 1913, **40**, 551.

[3] *D. p. G.*, 1913, **15**, 451.

[4] Planck, "Theorie der Wärmestrahlung," 1921, p. 127.

where $a = h^2/8\pi^2 IkT$. Then $d\bar{U}_r/dT$ gives the contribution to C_v of *one* degree of freedom of rotation. Ehrenfest then assumed that for a molecule with two degrees of freedom the contribution would be $2d\bar{U}_r/dT$, and, by assuming a value of I, was able to reproduce Eucken's results fairly well. The curve of C_v^{int}, however, passed through a maximum before the equipartition value was reached at high temperatures. Other calculations[1] led to a similar result. Reiche[2] used a model with two degrees of freedom (free axis), and assumed that the various quantum states had different *à priori* probabilities, which were taken into consideration by introducing a " weight factor " p_n into the formula for w_n :

$$w_n = p_n \cdot e^{-U^{(n)}/kT} \Big/ \sum_0^\infty p_n \cdot e^{-U^{(n)}/kT}.$$

When certain quantum states were excluded ($p = 0$), and the weight $2n$ was assigned to the nth quantum, the curve rose steadily with the temperature. The rotationless state ($n = 0$) receives the weight zero, *i.e.*, does not exist, and this is regarded as evidence for rotation at the absolute zero.

The table below gives the values of C_v^{int} found experimentally by Eucken and those calculated (i.) by Einstein's formula with $\beta\nu = 430$; (ii.) by the Nernst-Lindemann formula with $\beta\nu = 570$; (iii.) by Nernst's formula with $a = 37$; (iv.) by Reich's formula.

TABLE OF MOLECULAR HEATS OF HYDROGEN (INTERNAL).

T.	C_v^{int} Obs.	C_v^{int} Calculated.			
		(i.)	(ii.)	(iii.)	(iv.)
40	0·00	0·00	0·04	0·10	—
50	0·03	0·02	0·11	0·16	0·008
80	0·16	0·26	0·43	0·35	0·18
100	0·44	0·51	0·67	0·44	0·44
196·5	1·41	1·34	1·33	0·74	1·46
273	1·86	1·61	1·60	0·91	—

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[1] Holm, *A. P.*, 1913, **42**, 1311; Weyssenhoff, *ibid.*, 1916, **51**, 285; Rotszajn, *ibid.*, 1918, **57**, 81; Planck, *D. p. G.*, 1915, **17**, 407; Fokker, *A. P.*, 1914, **43**, 810.

[2] *A. P.*, 1919, **58**, 657.

The energy of the hydrogen molecule has been considered from the point of view of Bohr's theory by T. Krüger.[1] He regards the hydrogen molecule as a minute gyrostat, the axis of which is the line joining the two positive nuclei, around which the two electrons are spinning in a perpendicular circular orbit midway between the nuclei. The result [2] is not wholly satisfactory if only two degrees of freedom are assumed, although Eucken's value of $\beta\nu$ is approximately found.

According to Bjerrum's theory,[3] molecular rotations appear as absorption lines in the infra-red spectrum, and it has been found [4] that the absorption spectrum of water vapour consists of two groups of lines, which agree with $I = 0{\cdot}96 \times 10^{-40}$ and $I = 2{\cdot}21 \times 10^{-40}$.

According to Bohr's theory the *angular momentum* is quantised, and the frequency is then $\nu_n = nh/4\pi^2 I$.[5]

The effect of oscillation and rotation combined in the same dipolar molecule is to produce absorption bands corresponding with the frequencies $(\nu_0 + \nu)$ and $(\nu_0 - \nu)$, where ν is one of the rotational frequencies in the very long-wave infra-red, and ν_0 the oscillation frequency.[6] There will therefore be two extra lines, equidistant from the line ν_0 in the absorption spectrum, due to each rotational frequency. Such lines have been found experimentally.[7] According to Imes the middle line (ν_0) is missing in the spectra of halogen hydracids, *i.e.*, the molecules always rotate.

138. Calculation of Chemical Constants from the Quantum Theory.—The calculation of the constant of integration in the equation of the reaction isochore [251] in terms of the sum of Nernst's chemical constants (333) was an appreciable step in advance in the theory of chemical affinity. But the equations so far given do not provide a complete solution of the problem of predicting, from purely thermal magnitudes (heats of formation and specific heats) and universal constants, the behaviour of materials when placed together under specified conditions in the absence of passive resistances. The final step was taken in the case of monatomic substances by Sackur and by Tetrode,[1] who were able to calculate (by methods which cannot be given here [2]) the value of i in terms of universal constants. If the temperature is reduced to such an extent that the atomic heat of the condensed phase becomes negligible in comparison with unity, then [330] becomes:

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[1] *A. P.*, 1916, **50**, 346; **51**, 450.

[2] Macdougall, *J. A. C. S.*, 1921, **43**, 23.

[3] Bjerrum, *D. p. G.*, 1914, **16**, 640, 737; *N. F.*, 1912, p. 90; Bahr, *P. M.*, 1914, **28**, 71; Goldhammer, *D. p. G.*, 1914, **16**, 707; Ehrenfest, *D. p. G.*, 1913, **15**, 451; Epstein, *D. p. G.*, 1916, **18**, 398; *P. Z.*, 1919, **20**, 289; Kemble, *P. R.*, 1916, **8**, 689; Reiche, *A. P.*, 1919, **58**, 657; Spence and Holley, *J. Opt. Soc. Amer.*, 1923, **7**, 169.

[4] Rubens, *B. B.*, 1913, p. 513; Eucken, *D. p. G.*, 1913, **15**, 1159; *Z. p. C.*, 1922, **100**, 159.

[5] Cf. Sommerfeld, "Atombau und Spektrallinien," 3 Aufl., 1922, p. 513; also references given in Kap. 7 of this treatise.

[6] Rayleigh, *P. M.*, 1892, **34**, 410; Bjerrum, *N. F.*, 1912, p. 90; A. Kratzer, *Z. P.*, 1920, **3**, 289, 460; G. Hettner, *Z. P.*, 1920, **1**, 345; E. S. Imes, *Astrophys. J.*, 1919, **50**, 251; A. Haas, *Z. P.*, 1921, **4**, 68; F. W. Loomis, *Astrophys. J.*, 1920, **52**, 248.

[7] E. von Bahr, *D. p. G.*, 1913, **15**, 731.

$$\ln p = -\frac{\lambda_0}{\mathrm{RT}} + 2{\cdot}5 \ln \mathrm{T} + i \quad . \quad . \quad . \quad . \quad [329]$$

since C_{pr} is zero for a monatomic substance, and the value of i is then given by:

$$i = \ln (2\pi m)^{3/2} k^{5/2} / h^3 \quad . \quad . \quad . \quad . \quad . \quad (370)$$

where m is the mass of the atom, k is Boltzmann's constant (R/N_0, where N_0 is Avogadro's constant), and h is Planck's constant.[3] With numerical values (see below), and p in atm., this gives:

$$\mathrm{C} = -1{\cdot}589 + 1{\cdot}5 \log \mathrm{M} \quad . \quad . \quad . \quad . \quad . \quad (371)$$

where M is the atomic weight, referred to the same standards as N_0. ($k = 1{\cdot}37 \times 10^{-16}$; $h = 6{\cdot}55 \times 10^{-27}$; $\mathrm{N}_0 = 6{\cdot}06 \times 10^{23}$; 1 atm. = 1013250 abs. units.[4])

On the assumption that free electrons may be regarded as a monatomic gas (*gaz plus que parfait*, electrons mutually repelling one another), then $\mathrm{C}_p = 5/2 \,.\, \mathrm{R}$, and the chemical constant may be calculated by (370) or (371) with $\mathrm{M} = 0{\cdot}000544$: $\mathrm{C} = -1{\cdot}589 + 1{\cdot}5 \log \mathrm{M} = -6{\cdot}4856$. Substituting in [340], we obtain the relation:

$$\log \mathrm{K} = -\frac{\mathrm{Q}_0}{4{\cdot}576\mathrm{T}} + 5/2 \,.\, \log \mathrm{T} - 6{\cdot}486$$

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[1] Sackur, *A. P.*, 1911, **37**, 958; 1913, **40**, 67; Tetrode, *ibid.*, **38**, 434; 1912, **39**, 255; Stern, *A. P.*, 1914, **44**, 497; *Z. E.*, 1919, **25**, 66; Bródy, *Z. P.*, 1921, **6**, 79.

[2] Statistical mechanics: see Planck, "Theorie der Wärmestrahlung," 4 Aufl.; Tolman, *J. A. C. S.*, 1920, **42**, 2506; 1922, **44**, 75; *P. R.*, 1918, **11**, 261; Adams, *J. A. C. S.*, 1921, **43**, 1251; Fowler, *P. M.*, 1923, **45**, 497; Schottky, *P. Z.*, 1921, **22**, 1; Wereide, *P. Z.*, 1916, **17**, 62, 68.

[3] On chemical constants (including diatomic gases), cf. Latimer, *J. A. C. S.*, 1921, **43**, 819; Tolman, *ibid.*, 1921, **43**, 866, 1592; Eastman, *ibid.*, 1923, **45**, 80; Schames, *P. Z.*, 1920, **21**, 38; Brôdy, *Z. p. C.*, 1921, **6**, 79; Herzfeld, *P. Z.*, 1921, **22**, 186; Planck, *B. B.*, 1916, 653; Sackur, *A. P.*, 1911, **36**, 958; 1913, **40**, 67, 87; Schottky, *P. Z.*, 1921, **22**, 1; Stern, *P. Z.*, 1913, **14**, 629; *A. P.*, 1914, **44**, 497; Partington, *P. M.*, 1922, **44**, 988; 1923, **46**, 329.

[4] See Millikan, *P. M.*, 1917, **34**, 1.

which gives the degree of ionisation of elements at any temperature and pressure when the ionising potential is known.[1]

Example.—Calculate the degree of ionisation of cæsium vapour at 10,000° K. and 1 atm. pressure, given that the ionisation potential of Cs vapour is 3·9 volts.

If p is the pressure in atmospheres and x is the degree of ionisation, $\log px^2/(1 - x^2) = \log K$. Expressing the ionisation potential in calories, we have ($p = 1$):

$$\log x^2/(1 - x^2) = -\frac{3\cdot9 \times 23\cdot06 \times 10^4}{4\cdot576 \times 10{,}000} + \frac{5}{2}\log 10{,}000 - 6\cdot486$$

$$= \overline{17}\cdot864$$

$$\therefore \quad x = 8\cdot5 \times 10^{-7}\% \text{ nearly.}$$

139. Gases at Very Low Temperatures.—A direct application of the quantum theory to the energy of gases at very low temperatures has been made by Nernst,[2] who starts with two assumptions: (1) every gas when cooled at constant volume without condensation reaches ultimately a state of vanishingly small heat capacity; (2) the diminution in heat capacity with fall in temperature occurs more rapidly the greater the density of the mass of gas taken.

This theory is, however, regarded as much more hypothetical than the quantum theory of solids, and in any case the deviations from the gas laws would be appreciable only at very low (unattainable) temperatures.

EXAMPLES XVIII.

1. Calculate the specific heat of Zn ($\beta\nu = 160$) at 130° C., 280° C. and 360° C., from Einstein's formula.

2. For MgO ν (Debye) $= 160\cdot703 \times 10^{11}$ and ν (Einstein) $= 115\cdot5055 \times 10^{11}$. Calculate the molecular heat of MgO at the following temperatures according to the formulæ of both Debye and Einstein. The observed figures are due to Günther (1916).

	(a)	*(b)*	*(c)*	*(d)*	*(e)*
T° K. . . .	39·2	42·6	52·7	65·8	81·2
C_v obs. . . .	0·038	0·095	0·151	0·391	0·982

3. The frequency for copper ν (Debye) $= 658\cdot281 \times 10^8$. Calculate the atomic heat of copper at 69·66° K. and 89·38° K., using Debye's formula.

4. Calculate the atomic heat of copper at 20·88° K. by the Debye formula and the Nernst-Lindemann formula, given $\beta\nu$ (Debye) $= 323\cdot5$ and $\beta\nu$ (N. L.) $= 321$.

5. Calculate the atomic heat of aluminium at 40° K. $\beta\nu$ (Debye) $= 88$.

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[1] See Nernst, "Grundlagen," 1918, p. 154; Eggert, *P. Z.*, 1919, **20**, 570; Saha, *P. M.*, 1920, **40**, 472, 809, whose calculations are vitiated, however, by an error in the value of m; also A. A. Noyes and Wilson, *N. A.*, 1922, **8**, 303.

[2] "Grundlagen des neuen Wärmesatzes," 1918, pp. 154 ff.; *B. B.*, 1919, 118; cf. Planck, *ibid.*, 1916, 653; Sackur, *B.*, 1914, **47**, 1318; Keesom, *P. Z.*, 1913, **14**, 665; Sackur, *Z. E.*, 1914, **20**, 563; Sommerfeld, "Vorträge über die kinetische Theorie," Teubner, 1914, p. 126 ff.; Bródy, *Z. P.*, 1921, **6**, 79.

6. The following table gives the atomic heat of Ag at various temperatures:

T (abs.) =	35	45	77	100	200	215	242·4
C_v =	1·58	2·47	4·07	4·86	5·78	6·01	6·64

Plot the atomic heat against $T/\beta\nu$.

7. Find the approximate difference between C_p and C_v for lead at 23° K. and 85·5° K., given C_p at 23° K. = 2·96 and C_p at 85·5° K. = 5·65, the melting point of lead being 327° C.

8. The resonance potential of K is 1·55 volts, and the ionisation potential 4·1 volts. Find the frequency and wave-length of the resonance line and the energy of the limit of the principal ionisation series.

9. Calculate the wave-lengths of the first four lines of the Balmer series for hydrogen and compare with the following observed values: H_α = 6563, H_β = 4861, H_γ = 4340, H_δ = 4102 (all in Å units, 1 Å = 10^{-10} m.). Find also the wave-length of the series limit.

10. Assuming the atomic volume of a substance to be a linear function of the temperature calculate the atomic heat of iodine at 77° K., given that the atomic volume of solid I_2 is 25·99 at − 38·85° C. and 27·2 at 17° C. (Dewar), and the melting point is 114° C. (Use Nernst-Lindemann formula.)

11. The wave-length of the residual rays from NaCl was found by Rubens and Hollnagel as 61·1μ (μ = 10^{-4} cm.). Find the molecular heat at 0° C. according to Einstein's formula.

12. The compressibility of aluminium is 1·4 × 10^{-6} cm^2./kgm. wt., and the density 2·7, both at room temperature. Find the value of the frequency ν.

13. The density of iodine is 4·82 at the melting point 114° C. Find the atomic frequency.

14. Assuming one moment of inertia of the H_2O molecule to be 0·96 × 10^{-40}, calculate the wave-lengths in μ of the first four bands in the infra-red absorption spectrum.

15. Calculate the value of the chemical constant i for helium (atm. wt. = 4).

SYMBOLS USED IN THE TEXT

A	Work; sometimes atomic weight.
Å	Ångstrom unit = 10^{-10} metre.
A	Compressibility coefficient.
a	van der Waals' constant; also activity.
α	Coefficient of expansion; degree of dissociation; area.
b	van der Waals' constant.
β	Coefficient of pressure; also Nernst's quantum constant $= \frac{h\mathrm{N}_0}{\mathrm{R}} = 4{\cdot}77 \times 10^{-11}$.
C	Current in ampères.
C	Concentration ($= n/\mathrm{V}$).
$\mathrm{C}_1, \mathrm{C}_2, \ldots$	Concentrations of initial substances.
$\mathrm{C}_1', \mathrm{C}_2', \ldots$	Concentrations of products of reaction.
c	Specific heat; equilibrium concentration (with subscript); sometimes velocity of light.
$\bar{c}$	Mean specific heat.
C_p	Molecular heat at constant pressure.
C_v	Molecular heat at constant volume.
C	Conventional chemical constant.
D	Normal density.
d	Total (or complete) differential.
δ	Infinitesimal change.
Δ	Molecular depression.
∂	Partial differential; $(\partial y/\partial x)_z$ = partial differential coefficient of y with respect to x, z constant.
E	Electromotive force (E.M.F.); electrode potential; molecular elevation.
E_0	Electroaffinity.
e	Charge on the electron ($= 4{\cdot}774 \times 10^{-10}$ e.s.u.); sometimes the base of natural logarithms ($= 2{\cdot}718282$).
ϵ	Coefficient of elasticity.
ϵ_θ, ϵ_T	Isothermal coefficient of elasticity.
ϵ_Q	Adiabatic coefficient of elasticity.
η	Coefficient of compressibility.
F	Faraday's constant (= 96,500 coulombs when O = 16).
F	Free energy.
f	Function of; also activity coefficient; free energy per unit mass.
g	Acceleration of gravity = $981{\cdot}194$ cm./sec.^{2} at Kew.
γ	Ratio of specific heats.
γ_p, γ_v	Thermal coefficients.
Γ	Heat capacity; or adsorption excess.
H	Heat function at constant pressure (enthalpy).
h	Planck's constant ($= 6{\cdot}55 \times 10^{-27}$ erg sec.).
I	Integration constant of affinity equation; moment of inertia.
i	van't Hoff's coefficient; sometimes the chemical constant (§ 122).
J	Mechanical equivalent of heat.
K	Equilibrium constant ($= (c_1'^{n_1'} \times c_2'^{n_2'} \times \ldots)/(c_1^{n_1} \times c_2^{n_2} \ldots)$).
K	$= 1/\mathrm{K}$.
K'	Equilibrium constant ($= (p_1'^{n_1'} \times p_2'^{n_2'} \times \ldots)/(p_1^{n_1} \times p_2^{n} \times \ldots)$).
K'	$= 1/\mathrm{K}'$.
k	Distribution coefficient; Boltzmann's constant (gas constant per molecule) $1{\cdot}37 \times 10^{-16}$ erg/1° C.
L	Latent heat per gram.
L_e	Latent heat of evaporation per gram.
L_f	Latent heat of fusion per gram.

L_i	Internal latent heat per gram.
L_s	Latent heat of sublimation per gram.
l_a	Latent heat of surface extension per square centimetre.
l_p	Latent heat of pressure change.
l_v	Latent heat of volume change.
ln	Natural logarithm or $\log_e$; $\ln x = 2{\cdot}3026 \log x$.
log	Logarithm to base 10 or $\log_{10}$; $\log x = 0{\cdot}4343 \ln x$.
λ	(Limiting density of gas)/(normal density of gas); differential heat of saturation.
λ_e	Molar heat of evaporation.
λ_f	Molar heat of fusion.
λ_s	Molar heat of sublimation.
M	Molecular weight.
M	one mol (*i.e.*, one gram molecule).
m	Mass.
μ	Chemical potential per unit mass.
$\bar{\mu}$	Chemical potential per mol.
n, N	Number of mols.
N	Efficiency (= A/Q).
N_0	Avogadro's constant, *i.e.*, number of molecules in one mol of gas, $6{\cdot}06 \times 10^{23}$. (Loschmidt's number is the number per c.c.)
ν	Frequency.
P	Osmotic pressure or solution pressure.
p	Pressure.
$p_1, p_2, \ldots$	Partial pressures of initial substances of a reaction.
$p_1', p_2', \ldots$	Partial pressures of final substances of a reaction.
p_c	Critical pressure.
p_0	Vapour pressure of a pure liquid.
π	Reduced pressure $(= p/p_c)$; sometimes hydrostatic pressure.
ϕ	Reduced volume $(= v/v_c)$.
Q,q	Quantity of heat absorbed.
Q	Heat evolved (= − Q).
Q_x	Integral heat of solution.
Q_∞	Heat of dilute solution.
Q_d	Differential heat of dilution $(= \partial Q_x/\partial x)$.
Q_s	Differential heat of solution.
R	Molar gas constant (cf. § 34 for values).
ρ	Density.
ρ_c	Critical density.
s	Entropy per unit mass; sometimes concentration in gm./c.c., etc., as in §§ 90 ff.
S	Entropy.
σ	Surface tension.
Σ	Sum of.
$\int$	Integration.
$(\oint)$	Integration round a cycle.
T	Absolute temperature.
t	Time.
T_c	Critical temperature.
ϑ	Reduced temperature $(= T/T_c = 1/\tau)$.
τ	$T_c/T = \frac{1}{\vartheta}$.
θ	Temperature measured on any scale.
u	Intrinsic energy per unit mass.
U	Intrinsic energy.
u	Velocity of sound.
v, V	Volume.
V	Molar volume.
v_c	Critical volume.
W	Weight.
x_1, x_2	Generalised co-ordinates.
X_1, X_2	Generalised intensities.
y	Valency of ions.
z	Thermodynamic potential per unit mass; sometimes atomic number.
Z	Thermodynamic potential.

For very small quantities the following notation is sometimes used:—

$$0{\cdot}0_6 73 \equiv 0{\cdot}00000073 \equiv 73 \times 10^{-8}$$

and so on.

LIST OF ABBREVIATIONS

A.	Liebig's Annalen der Chemie (Leipzig).
A. A.	Verslagen en mededeelingen der Koninklijk Akademie van Wetenschappen (Amsterdam).
A. C. P.	Annales de Chimie et de Physique (Paris).
A. de P.	Annales de Physique (Paris).
A. G.	Archives des Sciences Physiques et Naturelles; Bibliotheque universelle de Genève (Geneva).
A. J.	American Journal of Science (New Haven).
A. L.	Atti della Reale Accademia dei Lincei (Rome).
A. N.	Archives Néerlandaises des sciences exactes et naturelles (Harlem).
A. P.	Annalen der Physik (Leipzig).
B.	Berichte der Deutschen chemischen Gesellschaft (Berlin).
B. B.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin (Berlin).
C. R.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences (Paris).
C. S.	Transactions of the Chemical Society (London).
D. p. G.	Verhandlungen der Deutschen physikalischen Gesellschaft (Leipzig).
E.	Elektrochemische Zeitschrift (Berlin).
F.	Journal of the Franklin Institute (Philadelphia).
F. S.	Transactions of the Faraday Society (London).
G.	Gazzetta chimica italiana (Rome).
" *Ges. Abh.* "	" Gesammelte Abhandlungen " (Collected Works).
" *H. M.* "	" Higher Mathematics for Chemical Students," by J. R. Partington (London, 1920).
J. A. C. S.	Journal of the American Chemical Society (New York).
J. C. P.	Journal de Chimie physique (Geneva).
J. P. C.	Journal of Physical Chemistry (New York).
J. P.	Journal de Physique (Paris).
M. B.	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg (Marburg).
M. K. N.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut (Upsala and Stockholm).
M. M.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society (Manchester).
N.	Nature (London).
N. A.	Proceedings of the National Academy of Sciences (Washington).
N. C.	Il Nuovo Cimento (Pisa).
N. F.	Nernst Festschrift (1912).
P. C. S.	Proceedings of the Chemical Society (London).
P. M.	The London, Edinburgh and Dublin Philosophical Magazine (London).
P. R.	The Physical Review (New York).

P. R. S.	Proceedings of the Royal Society of London (London).
P. T.	Philosophical Transactions of the Royal Society of London (London).
P. Z.	Physikalische Zeitschrift (Leipzig).
R. B. A.	Reports of the British Association for the Advancement of Science (London).
W.	Journal of the Washington Academy of Science (Washington).
W. B.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften zu Wien (Vienna).
Z. an. C.	Zeitschrift für anorganische und allgemeine Chemie (Hamburg and Leipzig).
Z. E.	Zeitschrift für Elektrochemie (Halle).
Z. P.	Zeitschrift für Physik (Berlin).
Z. p. C.	Zeitschrift für physikalische Chemie, Stöchiometrie, und Verwandschaftslehre (Leipzig).

ANSWERS TO EXAMPLES

Ex. I. (p. 8).—**1.** 0·12156 cals. **2.** 161·8 kg. cals. **3.** $\bar{c} = 0{\cdot}031590 + 2{\cdot}9234 \times 10^{-6}(T + T_0)$; $c_p = 0{\cdot}031590 + 5{\cdot}8468 \times 10^{-6}T$; c_p at 30° C. = 0·033362 nearly. **4.** 87,137 gm. cals. **5.** 0·2845 cals.; $C_p = 7{\cdot}0963 + 0{\cdot}0060896T - 0{\cdot}0_5 22022T^2$. **6.** Cu 0·093063; Pb 0·030379; Zn 0·09292; Cd 0·055784. **7.** 16·75 kg. cals. **8.** $C_p = 8{\cdot}6 + 0{\cdot}00957t$; 7·43 cals.; 1,911 cals. **9.** 8·995 cals. **10.** $\bar{C}_p$ (steam) $= 0{\cdot}449704 + 0{\cdot}0_4 33611\theta + 0{\cdot}0_7 11277\theta^2$; $\bar{C}_p$ at 350° C. = 0·473232. **11.** $2{\cdot}66 \times 10^{-4}$ gm. cals./atm. **12.** 67,921 gm. cals. **13.** 6·194 cals. **14.** 1058·4 kg. cals. **15.** 6·67 cals.; 12,130 cals.

Ex. II. (p. 17).—**1.** J = 42,445 gm. cms. Corrected for air resistance, this becomes 42,394 gm. cms. **2.** $J = 4{\cdot}216 \times 10^7$ ergs, or, corrected for a vacuum, $4{\cdot}212 \times 10^7$ ergs. If g = 981·3 cm./sec.^{2}, J = 42,923 gm. cms. **3.** 50,410 cals.; $2{\cdot}11 \times 10^{12}$ ergs. **4.** 3,806 cals. **5.** $5{\cdot}066 \times 10^9$ ergs; 121·08 gm. cals. **6.** 45·812 gm. cals.; $1{\cdot}9544 \times 10^6$ gm. cms. **7.** 385·90 gm. cals. **8.** $1{\cdot}7995 \times 10^{1}$ ergs. **9.** $9{\cdot}968 \times 10^{11}$ ergs. **10.** J = 43,702 gm. cms.

Ex. III. (p. 27).—**1,** $2{\cdot}735 \times 10^3$ ergs. **2.** 0·0145. **3.** $5{\cdot}08 \times 10^{-4}$ cal. per c.c.; 0·508 cal. **4.** 46·3 cals. **5.** 66·85 cals. **6.** 0·2839. **7.** $-[k\theta/(v - b)^2] + (2a/v^3)$. **8.** 0·376 c.c.; 9·081 c.c. **9.** $8{\cdot}825 \times 10^4$ gm. cal. per c.c. **10.** 2·414. **11.** — 12·47 cals. **12.** 740 g. cals.; 542 g. cals.

Ex. IV. (p. 32).—**1.** 118,000 cals. **2.** $QT = Q_0 + 0{\cdot}001T^2 = 12{,}010 + 0{\cdot}001T^2$; $Q_{727} =$ 13,010 cals. **3.** — 30·6 kg. cals. **4.** $Q_0 = 135{,}200$ cals.; $Q_{1000} = 136{,}680$ cals. **5.** $Q_V = 67{,}870 + 0{\cdot}60T - 0{\cdot}00065T^2 + 0{\cdot}0_6 55T^3$; Q_V at 1,000° C. = 68,600 cals. **6.** $Q_V = 10{,}012 - 0{\cdot}70\theta - 0{\cdot}0_3 45\theta^2$; Q_V at 800° C. = 9,164 kg. cals.; Q_V at 1,000° C. = 8,524 kg. cals.

Ex. V. (p. 43).—**6.** 55·3%. **7.** 1,484 cals. **8.** 0·38. **9.** $152{\cdot}3 \times 10^{-6}$ atm.$^{-1}$. **10.** 1·57. **11.** $c_v = 0{\cdot}05926$. **12.** $c_v = 0{\cdot}088406$; $c_p/c_v = 1{\cdot}109$. **13.** Simplification of the expression given shows that the relation between c_p and p is linear. 0·9; 1·00; 1·20. **14.** 0·033458105. **15.** 2,470 gm. cals. **16.** 0·0117 cal.; 0·0036 cal.; 0·0045 cal.

Ex. VI. (p. 55).—**1.** 3·41; 98·1. **2.** 890 cals.; 3,731 joules; $5{\cdot}805 \times 10^7$ gm. cals.; 36·93 litres; 0·3693 atm. **3.** $1{\cdot}35 \times 10^{10}$ ergs; $7{\cdot}86 \times 10^{10}$ ergs. **4.** (1) $5{\cdot}55 \times 10^{10}$ ergs; (2) $3{\cdot}42 \times 10^{10}$ ergs. **5.** $1{\cdot}0133 \times 10^9$ ergs; $1{\cdot}0333 \times 10^6$ gm. cms. **6.** $\gamma = 1{\cdot}4015$; γ (corr.) = 1·4027; $C_p = 6{\cdot}946$; $C_v = 4{\cdot}952$; $C_v{}^0 = 4{\cdot}948$. **7.** — 164·4° C. **8.** $C_p = 6{\cdot}82$; $C_v = 4{\cdot}83$. **10.** 1·42. **11.** 1·45. **12.** $C_p/C_v = 1{\cdot}000$; $u = 1{,}432$ m./sec. **13.** $\gamma = 1{\cdot}402$; γ (corr.) = 1·403; $C_p = 6{\cdot}95(3)$; $C_v = 4{\cdot}95(3)$. **14.** $C_p/C_v = 1{\cdot}302$; $C_v = 6{\cdot}758$; $C_p = 8{\cdot}799$. **15.** 43·659.

Ex. VII. (p. 66).—**1.** 4,940 cals. **2.** Cs: 18,300 cals. per mol; K: 20,750 cals. per mol; Na: 25,130 cals. per mol. **3.** 331 mm.; 178° C.; 40·2 cals./gm. **4.** Bertrand's Eqn.: p (in cms.) = 18·58, 22·13, 26·18, 30·60, 36·73, 42·12, 50·28, 58·91, 67·23, 78·25. Biot and Regnault's Eqn.: p (in cms.) = 18·58, 22·11, 26·13, 30·49, 36·67, 42·07, 50·23, 58·95, 67·48, 78·60. Kirchhoff's Eqn.: p (in cms.) = 18·58, 22·11, 26·12, 30·47, 36·64, 42·03, 50·21, 58·90, 67·46, 78·60. **5.** Biot and Regnault's Formula: p (in cms.) = 34·93, 41·68, 48·47, 54·05, 60·80, 66·84, 74·34. Bertrand's Formula ($n = 50$; cf. p. 60): p (in cms.) = 34·92, 41·72, 48·54, 54·12, 60·82, 66·84, 74·41. Kirchhoff's Formula: p (in cms.) = 34·94, 41·68, 48·49, 54·08, 60·81, 66·85, 74·34. **6.** 97·9 cals. **7.** L_e at 5°, 300 cals.; at 10°, 295 cals.; at 15°, 290 cals.; assuming gas laws L_e = 326 cals. **8.** 22,600 cals. **9.** 45·13° C.; 21·4 atm.; 17,005 cals. per gm. **10.** 0·0351° C. **11.** 3,460 cals. per mol H_2O; 930 cals. per mol H_2O. **12.** 0·423 cals. per gm. **13.** 14,880 cals. **14.** 14,660 cals. **15.** 8,196 cals. per mol. **16.** λ_s = 14,452 cals. **17.** c_v = 0·028; pressure increase = 60 atm. **18.** 97° C. **19.** Log. m = 8·789; log n = 3·3542.

Ex. VIII. (p. 91).—**1.** $a = 74 \times 10^5$; b = 61·0 referred to c.c. as unit of volume and 1 atm. as unit of pressure; R = 62·39; R = 82·09. **2.** a = 13895·8; b = 2·1155; units: 1 gm., 1 c.c., 1 atm. **3.** θ_c = − 145·92; p_c = 35·29 atm.; v_c = 3·96 c.c. per gm. **4.** b = 1·818; a = 3177·58 (units: gm., c.c., atm.); ρ_c = 0·1834 gm./c.c. **8.** H_2: a = 0·2108, b = 0·01975; N_2: a = 1·390, b = 0·03950; CO_2: a = 3·601, b = 0·04275; NH_3: a = 4·015, b = 0·03596; SO_2: a = 3·357, b = 0·02829 (units: gm., atm., litres). **9.** H_2: 93·9° C.; N_2: 36·9° C.; CO_2: 469° C.; NH_3: 710° C. **11.** 32·092. **12.** θ_c = 248·73° C. (obs. value = 318·73° C.); p_c = 45·74 atm.; a = 249·012; b = 0·449055 (units: atm., gm., c.c.). **14.** 0·2324. **19.** CCl_4: $L_e = 81{\cdot}75 - 0{\cdot}1013T$; n-$C_5H_{12}$: $L_e = 185{\cdot}64 - 0{\cdot}3125T$; $L_e = -39{\cdot}6 + 0{\cdot}687T - 0{\cdot}0_3893T^2$; Trouton's constants are 20·4, 20·7, 14·2, respectively.

Ex. IX. (p. 104).—**1.** Total pressure = 0·975 atm.; partial pressure N_2 = 0·76 atm.; partial pressure O_2 = 0·2 atm.; partial pressure of A = 0·0089 atm. **2.** 73·1 cals./gm. **3.** 199·5 cals./gm. **4.** 59·5 cals./gm. **5.** 214·97 cals./gm. **6.** 2·7° C. **7.** 2·15 atm.; a nearly 1% soln. (0·986 gm. per 100 gm. C_6H_6). **9.** 16·485 mm.

Ex. X. (p. 123).—**1.** 0·312 cals. per 1° C. **2.** 0·293 cals. per 1° C. **3.** 35·54 cals./1°C. **4.** 34·56 cals./1° C. **5.** 8·1 cals./1° C. **13.** 53·17 litre atm. **14.** 19·64 litre atm.; 61,424 cals. **15.** 28·83 lit. atm. **16.** − 5,498 cals.; − 4,758 cals. **20.** 17 cals./1° C. **22.** 0·01 cals./1° C. **23.** 11,920 cals. **24.** 390 cals. **26.** 4·991 cals. **27.** − 4·106 cals. **28.** $(\partial s/\partial T)_v = (1/T)(\partial u/\partial T)_v$ = 0·000304 cals. per 1° C. **29.** 6·12 cals. = $2{\cdot}56 \times 10^8$ ergs; conc. O_2 = 0·0084 mols/litre; partial pressure = 0·2 atm.; conc. N_2 = 0·034 mols per litre; entropy generated = $2{\cdot}11 \times 10^{-12}$ cals./1° C. = $8{\cdot}83 \times 10^5$ ergs/1° C. **30.** 0·3457 cals. **31.** $0{\cdot}0_4575$ atm. = 0·0437 mm. **32.** 92·32 gm. cals.; 0·347 gm. cals.

Ex. XI. (p. 136).—**1.** 15,630 joules. **2.** ΔU = 8,930 cals.; λ = 16,043 cals. **4.** 50,235 cals. **5.** 5,531·8 joules; 1322·1 gm. cals. **6.** − 16,000 cals. **7.** 65527·5 gm. cals. **11.** Solubility per 100 gms. water: 262·0 gms. at 50° C., and 189·8 gms. at 10° C.; observed values: 260·4 gms. and 190·5 gms. respectively. **12.** 6,880 gm. cals. **13.** 16·38 kg. cals. **16.** $Q = 332{\cdot}4 + 1{\cdot}365T - 4{\cdot}37\,.\,10^{-3}T^2 + 9{\cdot}72\,.\,10^{-6}T^3 - 8{\cdot}1\,.\,10^{-9}T^4$; 418 gm. cals.; 495 gm. cals.; $A = 332{\cdot}4 - 3{\cdot}143T \log T + 5{\cdot}677T + 4{\cdot}37\,.\,10^{-3}T^2 - 4{\cdot}86\,.\,10^{-6}T^3 + 2{\cdot}7\,.\,10^{-9}T^4$.

Ex. XII. (p. 140).—**2.** 1·02 cals./1° C. **4.** 4·53 cals./1° C. **5.** 0·304 cals. per 1° C. **6.** (a) $\Delta F = -2273 - 100S_0$ cals.; $\Delta Z = -2074 - 100S_0$ cals.; (b) $\Delta F = -3121 - 100S_0$ cals.; $\Delta Z = -3002$ cals. $- 100S_0$, where S_0 is an arbitrary entropy constant. **7.** $\Delta F = -3978 - 100S_0$ cals.; $\Delta Z = -3779 - 100S_0$ cals., S_0 being an arbitrary entropy constant. **8.** $\Delta F = -3978$ cals. $- 100S_0$; $\Delta Z = -3779$ cals. −

$100S_0$, S_0 being an arbitrary entropy constant. **10.** 1·61 lit. atm.; 1·61 lit. atm.

Ex. XIII. (p. 157).—**1.** 38,530 cals. **2.** (i.) 9,880 cals.; (ii.) 23·87% CO_2; 23·87% H_2; 26·13% H_2O; 26·13% CO; (iii.) about 650° C.; (iv.) 58,120 cals. **3.** Q = — 20,090 cals. Berthelot found – 21,600 cals.; 0·98%. **4.** 93,680 cals. per atom O_2. **5.** 44,000 cals. and 21,345 cals. **6.** 90,000 cals. per atom O_2. **7.** 2,940° K. **9.** 1,300 cals. **10.** 10,060, 12,280, 11,470 cals. absorbed; K at 900° = 0·2222. **11.** (i.) $8{\cdot}2 \times 10^{-30}\%$; (ii.) 53%. **12.** 42,520 gm. cals.; 747° C. **13.** 1,461 cals. per mol. **14.** (i.) $7{\cdot}31 \times 10^{-6}\%$; (ii.) $7{\cdot}31 \times 10^{-5}\%$; (iii.) 7·08%; (iv.) 1·77%; (v.) 42×10^{-27} atm.; (vi.) 2,500° K. **15.** 39 kg. cals. **16.** $Q = [6{,}582\,p\,(v - 20{\cdot}7)]/T$, where v = vol. of O_2 in c.c. per mol at p and T. **17.** 34,340 cals. **18.** 16,270 cals.; 17,260 cals. **19.** Q = – 86,883 cals.; – 43,480 cals.; $\ln K = 7 - (9{,}451/T)$; 46%.

Ex. XIV. (p. 183).—**1.** $0{\cdot}0_4819$. **2.** 15,930 cals. **3.** 0·116, 0·205, 0·196, 0·203. **4.** 0·1276 mols/litre. **5.** $m = 2$, $n = 1$, $k = 1{\cdot}47$ approx. **6.** 17·24 mm. **7.** 0·0109 gm. **8.** 0·0301. **9.** 6,828 cals. **10.** – 2·2 cals./1° (evolved). **11.** 107,100 cals. (absorbed). **13.** 29·25 cals.; $d \log (p_0/p)/dT = 0{\cdot}00136$; 14·73 cals.; $\partial \log (p/p_0)/\partial T = 0{\cdot}000684$. **14.** $Q_x = 760{\cdot}4683m - 10{\cdot}130416\,m^2 + 0{\cdot}0447491\,m^3$; $Q_d = \partial Q_x/\partial x = (1{\cdot}07007 - 0{\cdot}02851m + 0{\cdot}0001889m^2)(100 - m)^2$. **15.** For pure water $d \ln P/dT = Q/RT^2$; hence for a saturated solution $d \ln p/dT = (Q - l)/RT^2$. Now $T \ln P/p$ is a linear function of temperature; let $T \ln P/p = aT + b$, so that $\ln P/p = a + b/T$. By direct subtraction we have $d(\ln P/p)/dT = (d \ln P/dT) - (d \ln p/dT) = l/RT^2$. Comparing this with $d(\ln P/p)/dT$ obtained by differentiating $\ln P/p = a + b/T$, we see that $l = - bR$ = constant. **16.** 0·1243 c.c. **28.** 4·63, 0·808, 0·107. **30.** $\%C_6H_6$ = 68·5, 4%. **31.** 71·3%; 71·2%; 71·1%. **32.** 8·36, 19·90, 27·38, 36·46, 61·22% CCl_4. **33.** 16·5, 32·2, 59·2, 77·1; 94·4, molecular % C_6H_6. **34.** (i.) 12·23 cm.; (ii.) 1·6 cm.; (iii.) C_6H_5Cl 1·32 cm., C_6H_6 5·04 cm. **35.** 27 mm.; 4 water to 1 nitrobenzene. **36.** 0·596 mol C_6H_5Cl + 0·404 mol C_6H_5Br; (a) 0·0137 and 0·9863; (b) 0·9927 and 0·0073; 0·67 mols bromide to 0·33 mols chloride. **37.** 0·82; 0·14. **39.** $C_1C_2^{-0{\cdot}59} = 0{\cdot}39$. **40.** 90·23° C. **41.** Molecular % C_6H_6 in mixture of maximum vapour pressure = 8·35; vapour pressure of this mixture = 308·43 mm. P = 272·1, 277·0, 281·0, 285·8, 288·4, 293·9, 301·1, 304·9, 307·0 mm. **42.** P = 760·4, 759·3, 759·3 mm. **43.** 142·16° C., 73·64%.

Ex. XV. (p. 199).—**1.** CCl_4: – 42·539; Et_2O: – 35·056; C_6H_6: – 46·3; C_6H_5Cl: – 46·904; N_2: – 17·6; O_2: – 20·28; all in dynamical units. **2.** U in ergs:—CCl_4: – 30·319; Et_2O: – 21·006; C_6H_6: –27·14; C_6H_5Cl: – 39·764; N_2: – 9·33; O_2: – 4·03. **3.** 3·5 nearly. **4.** No. **5.** 1·99, hence liquid HI is a practically non-associated liquid. **6.** No. **7.** Diethyl tartarate: $\Gamma \times 10^{-10}$ = (a) 6·1460; (b) 5·7480; (c) 5·3660; (d) 4·4800; (e) 4·1090; (f) 3·1630; (g) 2·2900; (h) 1·6590; (k) 1·1140; (l) 0·6646. Diethyl malonate: $\Gamma \times 10^{-10}$ = (a) 12·6150; (b) 8·4590; (c) 6·9470; (d) 5·4470; (e) 4·4250; (f) 3·4160; (g) 2·2760; (h) 1·2090; (k) 0·7058; (l) 0·3350. Diethyl succinate: $\Gamma \times 10^{-10}$ = (a) 11·690; (b) 8·125; (c) 6·567; (d) 5·596; (e) 4·565; (f) 3·360; (g) 2·468; (h) 1·627; (k) 0·8958; (l) 0·4664. **8.** $n = 1$, $k = 0{\cdot}2$; $n = 3{\cdot}7$, $k = 0{\cdot}25$. **9.** $n = 1$, $k = 0{\cdot}15$; $n = 2{\cdot}1$, $k = 0{\cdot}2$. **10.** 184·79 mm.

Ex. XVI. (p. 211).—**1.** – 1,259 cals.; 9,500 joules per equivalent. **2.** (i.) 920·6 joules; (ii.) 7866·5 joules; (iii.) 5·43 cals.; (iv.) free energy change = heat of reaction = 7866·5 joules. **4.** $1{\cdot}0 \times 10^{-6}$ gm. ion per litre. **5.** 0·0014223 volt/1° C. **6.** + 0·1051 volt; + 0·1336 volt. **7.** 125,817 joules. **8.** Latent heat = – 69,360 joules; Δz = 275,920 joules; Q = 345,280 joules. **10.** – 66,600 joules/equivalent. **11.** 18,000 gm. cals. **12.** $\Delta z = 26{,}119$ cals.; $\Delta s = 11{\cdot}2$ cals./1° C.; $p_{AgCl} = 6 \times 10^{-40}$ atm. **13.** $+ 0{\cdot}0098$ volt; $- 0{\cdot}0051$ volt; 945·7 joules; 492·15 joules; **14.** $1{\cdot}6 \times 10^{-5}$ mols/lit.; 6×10^{-40} atm. **15.** (a) 819 joules; (b) 1,081 joules; (c) 455 joules; (d) 120 joules. **16.** Free energy decrease in joules :—(i.) at 25° C.: (a) 195,256, (b) 200,630, (c) 203,679, (d) 206,825, (e) 210,916; (ii.) at 30°: (a) 193,846, (b) 199,328, (c) 202,396, (d) 205,609, (e) 209,778; (iii.) at 35°: (a) 192,447, (b) 197,985, (c) 201,180, (d) 204,365, (e) 208,659. The value of $a \times 10^{6} =$ (a) $- 1448{\cdot}0$; (b) $- 1279{\cdot}0$; (c) $- 1274{\cdot}0$; (d) $- 1133{\cdot}4$; (e) $- 1087{\cdot}5$. The value of $\beta \times 10^{6} =$ (a) $+ 1{\cdot}0$, (b) $+ 3{\cdot}8$, (c) $+ 4{\cdot}7$, (d) $- 4{\cdot}7$, (e) $+ 1{\cdot}7$. Heat content decrease at 25° C. in joules: (a) 279,527, (b) 277,130, (c) 281,036, (d) 276,711, (e) 279,296. **17.** A, 0·155; B, 0·0915; C, 0·1625; D, 0·061. **18.** 2·63 volts; 1·86 volts. **19.** Yes; $E = - 0{\cdot}5632$ and $- 0{\cdot}5640$ volt respectively. The observed E for Cu metal $\longrightarrow Cu^{\cdot\cdot} = - 0{\cdot}5640$ volt. **20.** 12,348 cals.

Ex. XVII. (p. 232).—**1.** At $- 5°$, $A = 1{\cdot}4$ cal.; at $- 20°$, $A = 5{\cdot}6$ cal. **3.** 5·2%. **4.** 0·1 mm. **6.** (a) $3 \log x = - 25200/T + 1{\cdot}75 \log T - 0{\cdot}9$; (b) $3 \log x = - 25200/T + 1{\cdot}75 \log T - 1{\cdot}2$; % dissociation = 0·0012, 0·0090, 0·040, 0·88. **8.** 1403° K.; obs. 1428° K. **9.** 632° K.; obs. 600° K. **10.** 0·648 volt. **11.** 4,180 cals. per mol. **12.** $A = - 130 + 0{\cdot}0044T^{2}$.

Ex. XVIII. (p. 260).—**1.** 0·0899, 0·09056, 0·09071. **2.** Einstein = (a) 0·0005, (b) 0·0024, (c) 0·0180, (d) 0·099, (e) 0·307. Debye = (a) 0·038, (b) 0·095, (c) 0·1505, (d) 0·291, (e) 0·558. **3.** (i.) 2·57, (ii.) 3·43. **4.** (i.) 0·1249, (ii.) 0·080. Observed value at 20·88° K = 0·1247. **5.** 4·73. Observed value 4·72. **7.** 0·0097, 0·097. **8.** $\nu = 3{\cdot}771 \times 10^{6}$; $\lambda =$ 7955 Å units; $6{\cdot}53 \times 10^{-12}$ ergs. **9.** 6,604, 4,824, 4,369, 4,129; 3,670 Å. **10.** 4·394. **11.** 5·598. **12.** $6{\cdot}7 \times 10^{12}$. **13.** $1{\cdot}64 \times 10^{12}$. **14.** 10·8, 11·6, 12·4, 13·3 μ. **15.** 0·69.

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